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13. ABSTRACT *(Maximum 200 words)*

Our work provides an understanding of epitaxial growth at the atomic level and develops new phenomenological theories describing epitaxy on large space and time scales. It is hoped that a better understanding of crystal growth will allow us to optimize performance of solid state electronic devices and perhaps suggest how to grow new structures, with new functions.

During this funding period, we have focused our efforts on understanding two-dimensional growth in which the deposited material spreads rapidly on the surface and the crystal is grown layer-by-layer. We have proposed a new mechanism for surfactant action, proposed a set kinetic mechanism for the early stage of Si deposition on Si(100), and have elucidated the mechanism of island-shape changes. We have shown that the growth of heterogeneous systems is very complex and requires shape-dependent diffusion constants. We have performed thermodynamic and kinetic studies of the mean island shape and its surface tension. We have proposed a new thermodynamic theory of evaporation rate. We have clarified many aspects of the coarsening process and made some advances in the theory of rate constants.

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"Computer Simulations of Growth Phenomena on Solid Surfaces"

(a) List of Objectives

Our work provides an understanding of epitaxial growth at the atomic level and develops new phenomenological theories describing epitaxy on large space and time scales. There are practical reasons for seeking such an understanding. Solid state electronics is moving relentlessly toward smaller and smaller devices to increase both storage density and computing speed and to reduce power consumption. As devices get smaller and the surface-to-bulk ratio diminishes, the quality of the interface becomes very important. A rough interface degrades conductivity and luminescence and increases energy loss. Until now, progress in the growth of small and complex solid state structures has relied on empirical research. It is hoped that a better understanding of crystal growth will allow us to optimize device performance and perhaps suggest how to grow new structures, with new functions.

(b) Status of the Research Effort

We could grow a perfect solid if we could grow a perfect layer on the substrate and then grow the solid one layer at a time. This is why a lot of theoretical and experimental effort goes into studying sub-monolayer growth. Our results in this direction are described below.

(1) *A new mechanism for surfactant action.* Many experimental studies have shown that one can use "surfactants" to improve the quality of epitaxially grown films. These findings are especially important in the case of heteroepitaxy where lattice mismatch often leads to rough and fractured films. It is very likely that surfactant action has several mechanisms that depend on the chemical nature of the system. We have proposed and tested[3] one such mechanism, which is operative when the surfactant atoms repel those of the material being grown. This repulsion changes the character of the atomic motion from diffusion to a slower motion that we call "anomalous diffusion". This in turn increases the number of islands nucleated, as compared to the case when no surfactant is present, which leads to layer-by-layer growth. We established this mechanism by analysis and computer simulations, and have shown that it does explain the experimental observations. This is a new concept in epitaxy, likely to also be useful in the kinetics of surface reactions.

(2) *The kinetics of dimers in the early stage of epitaxy on Si(100).* In the past several years we have mapped the kinetic pathways followed by the first Si atoms deposited on a Si(100) surface and indicated how our results can be tested by low-temperature STM measurements. Recent

developments in technology have made such measurement possible. They confirmed our early predictions as well as those made prior to the experiments.[2] We have predicted that the Si atoms deposited on the surface will adsorb on top of the dimer rows, will move very rapidly along them, and will meet and make dimers and longer one-dimensional clusters on top of the rows. At higher temperatures the deposited atoms will move between the rows. We have also predicted that the dimers on top of the rows will rotate. These predictions were rather radical at the time they were made. The diffusion rate given by us was much larger than that *inferred* from experiments and the clusters we predicted were oriented perpendicular to the ones observed at high temperature. Nevertheless all our predictions were confirmed by detailed direct experiments.

We have also analyzed[6] the collective properties of missing dimers on Si(100) and predicted that they will form wavy lines on the surface. These have been detected by Zandvliet in Holland and their properties agree with those calculated by us.

(3) *Island shapes, evaporation, and coarsening.* The adsorbate islands formed on surfaces have very intriguing shapes. The equilibrium shape is a thermodynamic quantity that depends on the "surface" tension along the island's border. In principle, by analyzing these shapes we can calculate this tension. We have developed the methodology[7-9,11] of doing so in two cases: when the shape is determined by transport of material along the border, and when it is dominated by evaporation/condensation on the island. We have shown in both cases how one could use the measured shape to determine the edge tension. The evaporation of atoms from the islands leads to "coarsening": a change in island density and size distribution. In catalysis this is a highly obnoxious event which degrades the performance of the catalyst and needs to be avoided. In microelectronics it is a desirable effect since it can be used to make island sizes more uniform. We have developed new methods to simulate coarsening and in the process have studied the evaporation from islands in detail.[9,11] We discovered that the evaporation rate has strange properties and explained their origin. We have also shown that island coalescence follows a scaling law[13] which we have tested by simulations.

(4) *Growth of heterogeneous systems.* A system is heterogeneous if the lattice of the top layer is mismatched with that of the substrate. A good example is Au on a Au(100) surface.[14] Instead of making a square lattice (as would be expected on a (100) substrate), the top Au layer has a nearly hexagonal packing and its density is 20% higher than that of the bulk. The islands grown on this surface are rectangular and show a "size quantization": they tend to be six, or twelve, or eighteen atoms wide. We have used an effective medium theory to calculate the activation barriers for atom motion on and around the islands, to discover the reasons for the quantization of size and the preference for long rectangles. The bond length between the gold atoms on the top layer is shorter than in the bulk. The atoms tend to get close to each other in the horizontal direction and to

A Directed Algorithm for Finding Potential Energy Functions, Materials Research Seminar, Institute for Theoretical Physics, University of California, Santa Barbara, May 27, 1997

Searching for Potentials and Bootstrapping Time Scales, UCSB Institute of Theoretical Physics Workshop on Interatomic Potentials and Linking of Scales, June 5-7, 1997

Activated Dynamics on Surfaces, Euroconference on Technical Advances in Particle-Based Computational Material Sciences "Computer Simulation of Rare Events and the Dynamics of Classical and Quantum Condensed Phase Systems", Lerici, Italy, July 7-18, 1997

No consultative or advisory functions

(f) No inventions or patent disclosures

buckle vertically, so that along one direction six atoms in the island fit on top of five atoms on the substrate. Because of this buckling the mobility of an atom across an island is low, and the mobility along an island is high. This leads to growth of long islands. Moreover, the diffusion constant of an atom along the long edge of a rectangular island depends on the size of the island and is fastest if the island is six, twelve, or eighteen atoms wide. Once an island reaches one of these widths the atoms reaching its border move rapidly along the long edge of the rectangle, and reach the short edge and get stuck there. This mechanism favors both the long rectangle shape and size quantization. We are convinced that this mechanism (size-dependent mobility across the island or along its edges) is essential in understanding growth in heterogeneous systems.

(5) *Thermodynamic and kinetic studies of the mean island shape and its surface tension.* The thermodynamics and the kinetics of the small islands grown on a solid surface are fascinating because of the smallness of the system. If we think of such an island as a large molecule, which it is, then STM pictures of evolving islands provides us with information on the isomerization of a molecule in contact with an energy reservoir. Thermodynamics has been developed to deal with the mean properties of a huge number of molecules. What is then the meaning of thermodynamics when applied to measurements that study one island? The next question is how to implement thermodynamics to study a system in which all measurements are kinetic and we cannot measure the two essential quantities, work and heat. We have addressed this question in two lectures at the NATO school[10] in Rhodes. We proposed that the thermodynamic theory is meaningful only if it deals with averages over an ensemble of islands. We showed how such an ensemble can be constructed by performing kinetic measurements or simulations. This has been applied, in conjunction with kinetic Monte Carlo simulations, to determine the surface tension of the island's edge from its equilibrium with a gas of atoms adsorbed on the substrate, and also from the evolution of its shape. The results of these two independent theories are consistent with each other.

(6) *A thermodynamic theory of evaporation rate.* In work sponsored by this grant, we made a surprising discovery: the rate of evaporation of atoms from an island is proportional to $N^{0.36}$, where N is the number of atoms in the island. The exponent was independent of all other variables in the system, temperature, size, and kinetic model. Everyone in the field expected the exponent to be 1/2. To understand this size dependence we developed a theory of the evaporation rate[9] which predicts that the evaporation rate is proportional to $N^{1/2} \exp[\, b/N^{1/2}]$. This is even more surprising and seems to contradict our earlier results. However, both functional forms (i.e. $N^{0.36}$ and $N^{1/2} \exp[\, b/N^{1/2}]$) fit the data equally well! The constant b in the second equation depends, in a known way[9], on the edge tension of the island. By performing simulations of

evaporation rates we extracted b and the surface tension. The latter agrees very well with the surface tension extracted from simulations of island-vapor equilibrium[19], proving that our theory is sound.

(7) *Aspects of the coarsening process.* If we grow an ensemble of islands and they do not have the desired size or position distribution, we have one more chance: by heating the system we can cause the atoms of the islands to evaporate, move on the substrate, and join other islands. Heating also causes the islands to move along the surface, meet each other, and merge. This process, known as coarsening, will change the island-size distribution and the way the islands are arranged in space. We have studied, by Kinetic Monte Carlo simulations, the mobility of the islands and the change in island-size distribution caused by coarsening. It was proposed in the literature, by many authors, that the diffusion coefficient of a migrating island has a power-law dependence on the size, with a universal exponent (i.e. independent of material or working conditions). Our simulations[18] show that this is not the case. Recent experiments in Wendelken's group have confirmed our findings. We have also developed a phenomenological theory of the coarsening process taking place during deposition, as the islands grow in size, touch, and merge. We found a new scaling law for island-size distribution and confirmed it by simulations.

(8) *The theory of rate constants.* Kinetic simulations require the computation of a large number of rate constants. Activated complex theory is a favorite method for determining the rates. Such calculations have two difficult steps: finding the transition state and convincing oneself that the transition state approximation is correct. We have proposed a new procedure for finding transition states. This used a genetic programming method to "teach" the *ab initio* program the configurations for which to calculate energy to find the transition state most efficiently.[17] We have also studied a variational method for finding the best dividing surface for the transition state, in complex systems that have multiple recrossings.[16]

(c) Publications stemming from work performed under the grant

1. Evolution to Equilibrium of the Shape of an Island Formed by the Aggregation of Adsorbed Atoms, H. Shao, S. Liu, and H. Metiu, *Phys.* Rev. B 51, 7827 (1995)
2. Energetics and Dynamics of Si Ad-Dimers on Si(001), Z. Zhang, F. Wu, H. J. W. Zandvliet, B. Poelsema, H. Metiu, and M. G. Lagally, *Phys. Rev. Lett. 74*, 3644 (1995)
3. Submonolayer Growth with Repulsive Impurities: Island Density Scaling with Anomalous Diffusion, S. Liu, L. Bönig, J. Detch, and H. Metiu, *Phys. Rev. Lett. 74*, 4495 (1995)
4. The Kinetics of H_2 Dissociative Chemisorption: The Role of Transients, C. Chakravarty and H. Metiu, *J. Chem. Phys. 102*, 8643 (1995)

5. The Effect of Small-Cluster Mobility and Dissociation on the Island Density in Epitaxial Growth, S. Liu, L. Bönig, and H. Metiu, *Phys. Rev. B 52*, 2907 (1995)
6. Missing-Dimer-Vacancies Ordering on the Si(100) Surface, P. C. Weakliem, Z. Zhang, and H. Metiu, *Surface Sci. 336*, 303 (1995)
7. Evaporation of Single Atoms from an Adsorbate Island or a Step to a Terrace: Evaporation Rate and the Underlying Atomic-Level Mechanism, H. Shao, P. C. Weakliem, and H. Metiu, *Phys. Rev. B 53*, 16041 (1996)
8. Interlayer Diffusion and Motion of Adatoms in the Vicinity of Steps, S. Liu and H. Metiu, *Surface Sci. 359*, 245 (1996)
9. The Evaporation Rate of a One-Atom-High Island on a Solid Surface: A Thermodynamic Theory of the Size Dependence, H. Metiu and G. Rosenfeld, *Surface Sci. Lett. 373*, L357 (1997)
10. Obtaining Thermodynamic Information from Kinetic Measurements: Island Shape, Evaporation, and Coarsening, H. Metiu, to be published in *Surface Diffusion: Atomistic and Collective Processes*, M. Tringides, editor, Plenum (1998)
11. Kinetic Simulations of the Equilibrium between a Two-Dimensional Adsorbate Island and its Vapor: Shape, Vapor Pressure, and Surface Tension, L. Möllnitz, J. Jacobsen, J. Norskov, and H. Metiu, in preparation
12. A Kinetic Model for Island Shape Variations Under Epitaxial Conditions, S. Liu and H. Metiu, *Surface Sci. Lett.*, to appear
13. Quantum Size Effects on the Pattern Formation of Monoatomic-Layer-High Metal Islands at Surfaces, K-J. Jin, G. D. Mahan, H. Metiu, and Z. Zhang, *Phys. Rev. Lett. 80*, 1026 (1998)
14. An Effective Medium Theory Study of Au Islands on the Au(100) Surface: Reconstruction, Adatom Diffusion, and Island Formation, L. Bönig, S. Liu, and H. Metiu, *Surface Science 365*, 87 (1996)
15. The Effect of Island Coalescence on Island Density During Epitaxial Growth, S. Liu, L. Bönig, and H. Metiu, *Surface Sci. Lett. 392*, L56 (1997)
16. The Reaction Rate Constant in a System with Localized Trajectories in the Transition Region: Classical and Quantum Dynamics, D. Makarov and H. Metiu, *J. Chem. Phys. 107*, 7787 (1997)
17. Fitting Potential Energy Surfaces: A Search in the Function Space by Directed Genetic Programming, D. E. Makarov and H. Metiu, *J. Chem. Phys.*, to appear
18. Island Migration Caused by the Motion of the Atoms at the Border: Is There a Scaling Law?, A. Bogicevic, S. Liu, J. Jacobsen, B. Lundqvist, and H. Metiu, *Phys. Rev.B15 (Rapid Communications)*, to appear

19. Thermodynamics and Kinetics of Two-dimensional Islands on Surfaces: A Simulation Study, Lone Møllnitz, Master's Thesis (1997), Niels Bohr Institute, University of Copenhagen (supervised by H. Metiu and J. Nørskov)
20. Migration of Hydrogen on a Solid Surface: The Physics of the Process and the Methodology, H. Metiu, *Proc. Fermi School on the Dynamics of Rare Events* (Lerici, July 1997)
21. Some Constraints Involving the Statistical Properties of Trajectories Run in the Monte Carlo Computation of a Rate Constant and Their Use in Improving and Testing the Quality of Sampling, D. E. Makarov and H. Metiu, *J. Chem. Phys.*, to appear

(d) Professional personnel supported by the grant

Mr. Alexander Bogicevic (visiting from Chalmers University), Dr. Lutz Bönig, Mr. John Detch (undergraduate), Dr. Shudun Liu, Dr. Dmitrii Makarov, Dr. Gregory Mills, Ms. Lone Møllnitz (visiting from the University of Copenhagen), Dr. Hongxiao Shao, Dr. Seokmin Shin, Dr. Paul Weakliem

(e) Interactions

Presentations at seminars, meetings, conferences

Seminars

Crystal Growth, Island Shapes and Nucleation, Technical University of Lausanne, December 1995

Crystal Growth, Island Shapes and Nucleation, University of Geneva, December 1995

Electrons in Zeolites, Centre d'Etudes Nucleaires de Grenoble, December 1995

The Properties of Electrons Solvated in Zeolites, Tel Aviv University, January 1996

Adsorbate Self-Aggregation: Kinetics and Thermodynamics, Joint Chemical Physics-Theoretical Physics Seminar, Fritz Haber Institute, Berlin, March 7, 1996

The Properties of Electrons Solvated in Zeolites, Freie Universität, Berlin, March 8, 1996

Adsorbate Self-Aggregation: Kinetics and Thermodynamics, Physics Department, Aarhus University, April 11, 1996

Adsorbate Self-Aggregation: Kinetics and Thermodynamics, Physics Department, Technical University of Denmark, Lyngby, April 16, 1996

The Properties of Electrons Solvated in Zeolites, University of Paris, Sorbonne, May 6, 1996

Lectures at Professional Meetings

The Electronic and Magnetic properties of Akali-Doped Zeolites, International Chemical Congress of Pacific Basin Societies, Honolulu, December 1995 (presented by Nick Blake)

An Investigation of the Electronic and Optical Properties of Sodium Clusters in Sodalite, International Discussion Meeting on Time-Dependent Quantum Mechanics of Many-Electron Systems, Bangalore, January 9-12, 1996

Adsorbate Self-Aggregation, Symposium on Reaction Dynamics at Surfaces, Orsted Institute, Copenhagen, March 1, 1996

Electrons in Zeolites, Plenary Lecture at the Annual Meeting of the German Zeolite Society, Berlin, March 5, 1996

The Electronic and Magnetic Properties of Alkali-Metal-Doped Sodalites, ACS National Meeting, New Orleans, March 1996 (presented by Nick Blake)

Kinetic Simulations of Island Formation During Epitaxial Deposition, AFOSR Contractor's Meeting, Colorado Springs, June 2, 1996

An Investigation of the Electronic and Optical Properties of Sodium Clusters in Sodalite, ACS National Meeting, Orlando, August 25, 1996

Two lectures at the NATO ASI Workshop on "Surface Diffusion: Atomistic and Collective Processes", Rhodes, August 27-September 6, 1996

(a) *Beating the Time Scale: Simulations of Femtosecond Events All the Way to Minutes of Real-Time Runs*

(b) *Diffusion Controlled Aggregation of Adsorbed Atoms: Island Densities, Shapes, Evaporation, and Coarsening*

Lectures on Surface Processes: (i) *Beating the Time Scale: Simulations of Femtosecond Events All the Way to Minutes of Real-Time Runs.* (ii) *Diffusion-Controlled Aggregation of Adsorbed Atoms: Island Densities, Shapes, Evaporation, and Coarsening* , NATO ASI Workshop on Surface Diffusion: Atomistic and Collective Processes, Rhodes, August 27-September 6, 1996

Lectures on Zeolites: *(i) Zeolites: Structure and Uses. (ii) Zeolites: Interaction Potentials. (iii) Isolated Electrons Solvated in Zeolites. (iv) The Properties of Fully Doped Zeolites: Semiconductors or Metals?*, Australian Summer School on Condensed Matter Physics, Canberra, January 10-31, 1997

Simulations of Epitaxial Growth, Seminar Lecture, Chemistry Department, Hong Kong University of Science and Technology, February 3, 1997

Initial Stages of Epitaxial Growth: Modeling and Simulations, Symposium on Epitaxial Growth, Materials Research Society Meeting, San Francisco, March 31-April 4, 1997

Thermodynamics and Kinetics of Small Adsorbate Islands Studied by KMC Simulations, ACS National Meeting, San Francisco, April 13-17, 1997

Simulations of Epitaxial Growth, Materials Science Seminar, Applied Physics Department, California Institute of Technology, May 14, 1997