A Final Technical Report

on

Templated self-assembly of nanostructures

DE-FG02-03ER46091

September 2003 to September 2006

by

Zhigang Suo
School of Engineering and Applied Sciences
Harvard University
617 495 3789, suo@seas.harvard.edu

Submitted to

Dr. **Tim Fitzsimmons**
U. S. Department of Energy
Division of Material Science
1000 Independence Avenue, SW
Washington D. C. 20585-1290
E-Mail:Tim.Fitzsimmons@science.doe.gov
Phone: (301) 903-9830
Fax: (301) 903-9513

SUMMARY

The DOE grant (DE-FG02-03ER46091 $352,000) to Harvard University, entitled Templated Self Assemble of Nano-Structures, was intended to cover the three-year period from September 2003 to September 2006.

A Ph.D. student, Wei Hong, was dedicated to this project. Wei Hong earned his Ph.D. in August 2006, and is now an assistant professor at The University of Iowa. The project has resulted in 10 publications [1-10].

SCEINTIFIC ACHIEVEMENTS

Programmable motion and patterning of molecules on solid surfaces. Adsorbed on a solid surface, a molecule can migrate and carry an electric dipole moment. A nonuniform electric field can direct the motion of the molecule. A collection of the same molecules may aggregate into a monolayer island on the solid surface. Place such molecules on a dielectric substrate surface, beneath which an array of electrodes is buried. By varying the voltages of the electrodes individually, it is possible to program molecular patterning, direct an island to move in a desired trajectory, or merge several islands into a larger one. The dexterity may lead to new technologies, such as reconfigurable molecular patterning and programmable molecular cars. This paper develops a phase field model to simulate the molecular motion and patterning under the combined actions of dipole moments, intermolecular forces, entropy, and electrodes.

Molecular assembly on cylindrical surfaces. The dipole-dipole interactions mediate through the electrostatic field in the space. If the space is shaped, the electrostatic field will be affected, and so will the molecular pattern. To illustrate this idea, we develop a model to evolve molecular pattern on the surface of a wire, or the inner surface of a tube. Molecules assemble into parallel rings on the wire, and parallel stripes on the internal surface of a tube. When the tube radius is comparable to, or smaller than, the island size, the stripes switch to the rings; occasionally, the stripes form spirals.

Persistent step-flow growth of strained films on vicinal substrates. This is a new direction for us, and the work is carried out in collaboration with an experimental group at the Oak Ridge National Labs. Many applications demand high-quality thin films of complex materials, yet proper choice of their growth conditions still largely relies on trial-and-error rather than a thorough understanding of the underlying mechanisms. We propose and experimentally verify a theory of persistent step flow, emphasizing dominant kinetic processes and strain effects. A morphological phase diagram is constructed, delineating a regime of step flow from regimes of step bunching and island formation. The theory also predicts the existence of concurrent step bunching and island formation, a new growth mode that competes with step flow for phase space. Furthermore, to achieve step flow on a substrate of a given terrace width, the deposition flux and temperature must be chosen within a window. The theory rationalizes the diverse growth modes observed in pulsed laser deposition of $SrRuO_3$ on $SrTiO_3$.

Nonlinear analyses of wrinkles in films on soft elastic substrates. Subject to compression in its plane, a film on a soft substrate often wrinkles. This paper reports on nonlinear analyses of the wrinkles. For an array of stripe wrinkles, the elastic energy is a fourth order polynomial of the wrinkle amplitude, so that the wrinkle instability behaves similarly to a phase transition of the second kind. The flat film becomes wrinkled when the magnitude of the membrane force exceeds a critical value. We obtain the equilibrium wrinkle wavelength and amplitude by minimizing the elastic energy. A spectral method is developed to simulate two-dimensional wrinkle patterns. Depending on the anisotropy of the membrane forces, the wrinkle

patterns can be stripes, labyrinths, or herringbones. Wrinkle patterns are also affected by the spatial distribution of the membrane forces. Statistical averages of the amplitude and wavelength of the random wrinkles correlate well with the analytical solution the stripe wrinkles.

Interplay between stress and kinetic effects in the step flow growth of oxide and semiconductor films. A vicinal Si (001) surface may form stripes of terraces, separated by monatomic-layer-high steps of two kinds, S_A and S_B. As adatoms diffuse on the terraces and attach to or detach from the steps, the steps move. In equilibrium, the steps are equally spaced due to elastic interaction. During deposition, however, S_A is less mobile than S_B. We model the interplay between the elastic and kinetic effects that drives step motion, and show that during homoepitaxy all the steps may move in a steady state, such that alternating terraces have time-independent, but unequal, widths. The ratio between the widths of neighboring terraces is tunable by the deposition flux and substrate temperature. We study the stability of the steady state mode of growth using both linear perturbation analysis and numerical simulations. We elucidate the delicate roles played by the standard Ehrlich-Schwoebel (ES) barriers and inverse ES barriers in influencing growth stability in the complex system containing (S_A+S_B) step pairs.

The following papers have been completed under the DOE support:

1. Wei Hong, Ho Nyung Lee, Mina Yoon, Hans M. Christen, Douglas H. Lowndes, Zhigang Suo, and Zhenyu Zhang, Persistent step-flow growth of strained films on vicinal substrates. Phys Rev Lett. 95, 095501 (2005).
2. Z.Y. Huang, W. Hong, Z. Suo, Nonlinear analyses of wrinkles in films on soft elastic substrates. The Journal of Mechanics and Physics of Solids, **53**, 2101-2118 (2005)
3. Z. Suo and W. Hong, Programmable motion and patterning of molecules on solid surfaces. *Proceedings of the National Academy of Sciences of the United States (PNAS)* **101**, 7874-7879 (2004).
4. Z. Suo, Y.F. Gao and G. Scoles, Nanoscale domain stability in organic monolayers on metals. *Journal of Applied Mechanics* 71, 24-31 (2004).
5. Z.Y. Huang, W. Hong, Z. Suo, Evolution of wrinkles in hard films on soft substrates. Phys. Rev. E. 70, 030601 (R) (2004).
6. W. Hong and Z. Suo, Molecular assembly on cylindrical surfaces. International Journal of Solids and Structures 41, 6895-6903 (2004).
7. M.E. Kassner, S. Nemat-Nasser, Z. Suo, G. Bao, J. C. Barbour, L.C. Brinson, H. Espinosa, H. Gao, S. Granick, P. Gumbsch, K.S. Kim, W. Knauss, L. Kubin, J. Langer, B.C. Larson, L. Mahadevan, A. Majumdar, S. Torquato, F. van Swol. New directions in mechanics. Mechanics of Materials. 37, 231-259 (2005).
8. W. Hong, Z.Y. Zhang and Z. Suo, Interplay between ed kinetic processes in stepped Si (001) homoepitaxy. Physical Review B 74, 235318 (2006).
9. Wei Hong, Zhigang Suo and Zhenyu Zhang, Dynamics of terraces on a silicon surface due to the combined action of strain and electric current„*Journal of the Mechanics and Physics of Solids* **56**, 267-278 (2008)
10. Mina Yoon, Ho Nyung Lee, Wei Hong, Hans M. Christen, Zhenyu Zhang, Zhigang Suo, Dynamics of step bunching in heteroepitaxial growth on vicinal substrates., Physical Review Letters 99, 055503 (2007).

Awards and honors

- Elected Fellow of American Society of Mechanical Engineers.
- Elected Chair of the Gordon Research Conference on Thin Film and Small Scale Mechanical Behavior.
- Elected Member of the Executive Committee of the Applied Mechanics Division of American Society of Mechanical Engineers.

IMPACT AND FUNTURE OUTLOOK

Mass-producing functional structures at the nanoscale is a great challenge of our time. Various self-assembly processes offer tantalizing promises as low cost, high throughput patterning techniques. However, both recent experimental observations and our own theoretical simulations have shown that self-assembly processes seldom produce perfect periodic structures, and never produce designed aperiodic structures. On the other hand, nature has produced proteins, polypeptides of specific, aperiodic sequences. The lesson, learned from our own frustration and from nature's solution, is to template the self-assembly. The proposed project builds on our accomplishments in modeling self-assembled monolayer patterns, and on our strength in solid mechanics, in which a large collection of tools are available to solve complex boundary value problems. To make definitive progress, our research focuses on a class of self-assembling systems (the monolayer on solid substrate). These systems exhibit rich phenomena, and are model systems to study a wide range of issues inherent in self-assembly. It is envisioned that our theory will not only explain the available experimental observations, but also motivate new experiments, especially in using various template mechanisms and unconventional substrates. The field is wide open.