

## **FINAL TECHNICAL REPORT TO THE DEPARTMENT OF ENERGY**

Title: Nanoscale Morphology Evolution Under Ion Irradiation

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## MAJOR ACCOMPLISHMENTS

- We showed that the half-century-old paradigm of morphological instability under irradiation due to the curvature-dependence of the sputter yield, can account neither for the phase diagram nor the amplification or decay rates that we measure in the simplest possible experimental system -- an elemental semiconductor with an amorphous surface under noble-gas ion irradiation.
- We showed that a model of pattern formation based on the impact-induced redistribution of atoms that do not get sputtered away explains our experimental observations.
- We developed a first-principles, parameter-free approach for predicting morphology evolution, starting with molecular dynamics simulations of single ion impacts, lasting picoseconds, and upscaling through a rigorous crater-function formalism to develop a partial differential equation that predicts morphology evolution on time scales more than twelve orders of magnitude longer than can be covered by the molecular dynamics.
- We performed the first quantitative comparison of the contributions to morphological instability from sputter removal and from impact-induced redistribution of atoms that are removed, and showed that the former is negligible compared to the latter.
- We established a new paradigm for impact-induced morphology evolution based on crater functions that incorporate both redistribution and sputter effects.
- We developed a model of nanopore closure by irradiation-induced stress and irradiation-enhanced fluidity, for the near-surface irradiation regime in which nuclear stopping predominates, and showed that it explains many aspects of pore closure kinetics that we measure experimentally.

## PATENTS ACKNOWLEDGING DOE SUPPORT

- "Tunable Nanometer Electrode Gaps by MeV Ion Irradiation"

## PUBLICATIONS ACKNOWLEDGING DOE SUPPORT

- M.J. Aziz, "Nanoscale Morphology Control Using Ion Beams", *Matematisk-Fysiske Meddelelser / udg. af Det Kongelige Danske Videnskabernes Selskab* **52**, 187 (2006); invited paper in Proceedings of the Ion 2006 Conference, P. Sigmund, ed.
- W.J. MoberlyChan, D.P. Adams, M.J. Aziz, G. Hobler, T. Schenkel, "Fundamentals of FIB Nanostructural Processing: Below, At and Above the Surface", *MRS Bulletin* **32**(5), 424-432 (2007). B. Davidovitch, M.J. Aziz, and M.P. Brenner, "On the Stabilization of Ion Sputtered Surfaces", *Physical Review B* **76**, 205420 (2007).
- K.Z. House, C.H. House, D.P. Schrag, and M.J. Aziz, "Electrochemical Acceleration of Chemical Weathering as an Energetically Feasible Approach to Mitigating Anthropogenic Climate Change", *Environmental Science and Technology* **41**, 8464 (2007).

- C.S. Madi, B. Davidovitch, H.B. George, S.A. Norris, M.P. Brenner, and M.J. Aziz, “Multiple Bifurcation Types and the Linear Dynamics of Ion Sputtered Surfaces”, *Physical Review Letters* **101**, 246102 (2008).
- K.Z. House, C.H. House, D.P. Schrag, and M.J. Aziz, “Electrochemical Acceleration of Chemical Weathering for Carbon Capture and Sequestration”, Proceedings of the Ninth International Conference on Greenhouse Gas Control Technologies, Washington DC, November 16-20, 2008. *Energy Procedia* **1**, 4953 (2009).
- B. Davidovitch, M.J. Aziz, and M.P. Brenner, “Linear Dynamics of Ion Sputtered Surfaces: Instability, Stability and Bifurcations”, *Journal of Physics: Condensed Matter* **21**, 224019 (2009).
- S.A. Norris, M.P. Brenner, and M.J. Aziz, “From Crater Functions to PDEs: A New Approach to Ion Bombardment Induced Nonequilibrium Pattern Formation”, *Journal of Physical Condensed Matter* **21**, 224017 (2009).
- C.S. Madi, H.B. George, and M.J. Aziz, “Linear Stability and Instability Patterns in Ion-Sputtered Silicon”, *Journal of Physical Condensed Matter* **21**, 224010 (2009).
- R. Asmatulu, A. Karthikeyan, D.C. Bell, S. Ramanathan, and M.J. Aziz, “Synthesis and Variable Temperature Electrical Conductivity Studies of Highly Ordered TiO<sub>2</sub> Nanotubes”, *Journal of Materials Science* **44**, 4613 (2009).
- H.B. George, Y. Tang, X. Chen, J. Li, J.W. Hutchinson, J.A. Golovchenko and M.J. Aziz, “Nanopore Fabrication in Amorphous Si: Viscous Flow Model and Comparison to Experiment”, *J. Appl. Phys.* **108**, 014310 (2010).
- H.B. George, D.P. Hoogerheide, C.S. Madi, D.C. Bell, J.A. Golovchenko and M.J. Aziz, "Ion Sculpting of Nanopores in Amorphous Metals, Semiconductors, and Insulators", *Appl. Phys. Lett.*, **96**, 263111 (2010).
- C.S. Madi, E. Anzenberg, K.F. Ludwig, and M.J. Aziz, "Mass Redistribution Causes the Structural Richness of Ion-Irradiated Surfaces", *Phys. Rev. Lett.* **106**, 066101 (2011); Erratum **110**, 069903.
- S.A. Norris, J. Samela, L. Bukonte, M. Backman, F. Djurabekova, K. Nordlund, C.S. Madi, M.P. Brenner, and M.J. Aziz, "Molecular Dynamics of Single-Particle Impacts Predicts Phase Diagrams for Large Scale Pattern Formation", *Nature Communications* **2**, 276 (2011).
- D.P. Hoogerheide, H.B. George, J.A. Golovchenko, and M.J. Aziz, “Thermal Activation and Saturation of Ion Beam Sculpting”, *J. Appl. Phys.* **109**, 074312 (2011).
- E. Anzenberg, C.S. Madi, M.J. Aziz, and K.F. Ludwig “Time-Resolved Measurements of Nanoscale Surface Pattern Formation Kinetics in Two Dimensions on Ion Irradiated Si”, *Phys. Rev. B* **84**, 214108 (2011).
- C.S. Madi and M.J. Aziz, “Multiple Scattering Causes the Low Energy-Low Angle Constant Wavelength Topographical Instability of Argon Ion Bombarded Silicon Surfaces”, *Appl. Surf. Sci.* **258**, 4112 (2012).
- J.-C. Cheang-Wong, K. Narumi, G.M. Schürmann, M.J. Aziz and J.A. Golovchenko, “Tunable Nanometer Electrode Gaps by MeV Ion Irradiation”, *Appl. Phys. Lett.* **100**, 153108 (2012).
- J.C. Perkinson, C.S. Madi, and M.J. Aziz, "Nanoscale Topographic Pattern Formation on Kr<sup>+</sup>-Bombarded Germanium Surfaces", *J. Vac. Sci. Technol. A* **31**, 021405 (2012).

- E. Anzenberg, J.C. Perkinson, C.S. Madi, M.J. Aziz, and K.F. Ludwig, Jr., "Nanoscale Surface Pattern Formation Kinetics on Germanium Irradiated by Kr<sup>+</sup> Ions", *Phys. Rev. B* **86**, 245412 (2012).
- M. Holmes-Cerfon, W. Zhou, A.L. Bertozzi, M.P. Brenner, and M.J. Aziz, "Development of Knife-Edge Ridges on Ion-Bombarded Surfaces", *Appl. Phys. Lett.* **102**, 143109 (2012).
- L. Bukonte, F. Djurabekova, J. Samela, K. Nordlund, S.A. Norris, and M.J. Aziz, "Comparison of Molecular Dynamics and Binary Collision Approximation Simulations for Atom Displacement Analysis", *Nucl. Instrum. Meth. B* **297**, 23 (2013).
- S.A. Norris, J. Samela, M. Vestberg, K. Nordlund, and M.J. Aziz, "Crater Functions for Compound Materials: A Route to Parameter Estimation in Coupled-PDE Models of Ion Bombardment", *Nucl. Instrum. Meth. B* **318**, 245-252 (2014).
- J.C. Perkinson, E. Anzenberg, M.J. Aziz, and K.F. Ludwig, "Model-independent Test of the Crater Function Theory of Surface Morphology Evolution During Ion Bombardment," *Phys. Rev. B* **89**, 115433 (2014).

### PRESENTATIONS ACKNOWLEDGING DOE SUPPORT

- An invited talk on this research was presented at the 2006 International Conference on Ion Beam Modification of Materials in September 2006.
- An invited talk on this research was presented at the 10th International Conference on Plasma Surface Engineering in Garmisch-Partenkirchen, Germany in September 2006.
- An invited talk on this research was presented at the University of Maryland Center for Materials Science of Nanostructures in October 2006.
- An invited talk on this research was presented at the MRS 2006 Fall Meeting at a joint session of Symposium N (Self Assembly of Nanostructures Aided by Ion- or Photon-beam Irradiation: Fundamentals and Applications) and Symposium LL (Focused Ion Beams for Analysis and Processing) in November 2006.
- An invited talk on this research was presented at the University of Virginia in March 2007.
- An invited talk on this research was presented at the MRS 2007 Spring Meeting Symposium GG (Ion Beam-based Nanofabrication) in April 2007.
- An invited talk on this research was presented at Boston University in December 2007.
- An invited talk on this research was presented at the Institute for High Performance Computing in Singapore in January 2008.
- An invited talk on this research was presented at the MRS 2008 Spring Meeting Symposium Y (Focused Ion Beams for Materials Characterization and Micromachining) in San Francisco in March 2008.
- An invited talk on this research was presented at the International Conference on Electronic Materials, Symposium L (Ion Beam Processing and Characterisation) in Sydney, Australia, in July 2008.
- An invited talk on this research was presented at the MRS 2009 Spring Meeting Symposium DD (Ion Beams and Nano-Engineering) in April 2009.

- An invited talk on this research was presented as Leader Participant at the Huntsville Ion Beam Institute in July 2009.
- An invited talk on this research was presented at the MRS 2009 Fall Meeting Symposium KK (Nanoscale Pattern Formation) in December 2009.
- An invited talk on this research was presented at the MRS 2010 Spring Meeting Symposium LL (Directed Assembly and Self Assembly - From Synthesis to Device Applications) in San Francisco in April 2010.
- A contributed talk by C.S. Madi was presented at the 17th International Conference on Ion Beam Modification of Materials in Montreal, Canada in August 2010. (The P.I. was on the international program committee of IBMM; consequently nobody in his group gave invited talks.)
- A poster by S.A. Norris was presented at the 17th International Conference on Ion Beam Modification of Materials in Montreal, Canada in August 2010.
- An invited talk on this research was the opening lecture of the Conference on Frontiers in Interface Physics: Microfluidics, Biomembranes and Nanostructures, Benasque, Spain, November 2010.
- A contributed talk by C.S. Madi was presented in MRS 2010 Fall Meeting Symposium T (Nanostructured Materials in Harsh Environments) in Boston in November 2010.
- A contributed talk by former researcher S.A. Norris was presented in MRS 2010 Fall Meeting Symposium R (Radiation Damage in Ceramic and insulating Materials for Nuclear Power) in Boston in November 2010.
- A contributed talk on our collaboration by collaborator E. Anzenberg was presented in MRS 2010 Fall Meeting Symposium UU (Real-time Studies of Evolving Films and Interfaces) in Boston in November 2010.
- An invited talk on this research was the keynote lecture at the International Conference on Ion-Beam Induced Nanopatterning of Materials in Bhubaneshwar, India, February 2011.
- An invited talk on this research was presented at the MRS 2011 Spring Meeting Symposium II (Ion Beams - New Applications from Mesoscale to Nanoscale) in San Francisco, April 2011.
- An invited talk on this research was presented at the E-MRS 2011 Spring Meeting Symposium LL (Ion Beam Synthesis and Modification of Nanostructured Materials and Surfaces) in Nice, France, in May 2011.
- An invited talk on this research was given by former postdoc S.A. Norris at the International Workshop on Nanoscale Pattern Formation at Surfaces that took place September 2011, in El Escorial, Spain.
- A contributed talk by Ph.D. student Joy Perkinson was presented in the MRS 2011 Fall Meeting Symposium EE (Self Organization and Nanoscale Pattern Formation) in Boston in November 2011.
- A contributed talk by former postdoc S.A. Norris was presented in the MRS 2011 Fall Meeting Symposium EE (Self Organization and Nanoscale Pattern Formation) in Boston in Nov. 2011.
- A contributed poster on our collaboration was presented by collaborator E. Anzenberg in the MRS 2011 Fall Meeting Symposium EE (Self Organization and Nanoscale Pattern Formation) in Boston in November 2011.

- An invited talk by M.J. Aziz was presented at the 2012 Conference on the Application of Accelerators in Research and Industry Symposium on Surface Nano-Pattern Formation in Fort Worth, TX in August 2012.
- A contributed talk by Ph.D. student J.C. Perkinson was presented at the 2012 Conference on the Application of Accelerators in Research and Industry Symposium on Surface Nano-Pattern Formation in Fort Worth, TX in August 2012.
- An invited talk on this research was presented at the Northeastern University Center for Interdisciplinary Research on Complex Systems in April 2013.
- A contributed talk on this research was presented at the International Symposium on Nanoscale Pattern Formation at Surfaces, Royal Danish Academy of Sciences and Letters in Copenhagen, Denmark in May 2013.
- An invited talk on this research was presented at the E-MRS (Symposium on Ion Beam Applications: New and Innovative Approaches) in Strasbourg in May 2013.
- An invited talk on this research was presented at the Conference on Particle-Surface Interactions from Surface Analysis to Materials Processing in Luxembourg in June 2013.
- An invited talk on this research was presented at the International Conference on Surface Modification of Materials Using Ion Beams in Kusadasi, Turkey, in September 2013.

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