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13. ABSTRACT *(MAXIMUM 200 WORDS)*

An atomic force microscope was acquired and used to study the surface properties of polymers and ceramics. Studies of polymers included nanomachining, mechanical properties, wetting behavior of latex, and metallization. Studies of ceramics included faceting of TiO_2, morphology of oxide fracture surfaces, heteroepitaxial oxide film growth, and oxidation of vanadium carbide.

A prototype instrument for use in ultra-high vacuum was designed.

14. SUBJECT TERMS

Atomic Force Microscope, ceramics, polymers, surface structure, thin films, adhesion, micromechanics

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DIRECT IMAGING OF THE SURFACE MICROSTRUCTURE OF DIELECTRIC MATERIALS USING AN ATOMIC FORCE MICROSCOPE

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The Atomic Force Microscope (AFM) was used for direct nanometer-scale resolution imaging and mechanical modification of polymer and ceramic surfaces. The effect of processing conditions on surface properties was also studied.

Major Achievements

1. Improvements in AFM Measurement Technology. We use the Park Instruments SFM-BD2 Force Microscope which was purchased during the first year of the grant. We have made several improvements to the AFM instrumentation and have established many of the physical limitations of the method.

- An AFM/STM laboratory has been established at the University of Maine. Samples can be analyzed in ambient air, in transparent fluids, and at temperatures up to 100 °C.
- Lateral resolution of AFM on polymers surfaces is limited by adhesive forces between the tip and substrate. Typical values for polyimide surfaces are about 150 Å and are in good agreement with values predicted by contact mechanics [v, reference number publication list below].
- Writing sub-micrometer wide line with the AFM has been demonstrated on polymer surfaces [ii].

- Quantitative information about the mechanical properties (Young's modulus, yield strength) of polymer surfaces can be extracted using the AFM [vi].
- A thermal stage has been developed that allows imaging at temperatures up to 100 °C [manuscript in preparation].
- An ultra-high vacuum AFM was designed based on experience gained in this AFOSR funded project. Construction is currently underway under funding from NSF.

2. Highlights of Research Results on Polymer Surfaces. Several clean and metal coated polymers have been studied. Major results include:

- Evaporated metals do not wet polyimides [iii,vi]. Rather, clusters nucleate and grow. Continuous films are formed only after about 50 Å thickness.
- The surface yield stress of PMDA-ODA is about 125 MPa [vii].
- Plastic deformation of PMDA-ODA results in volume increases [vii].
- Fine grooves in PMDA-ODA, such as those used in liquid crystal displays, are formed by plastic deformation rather than cutting to remove material [ii,vii].
- The number of inclusions with high mechanical strength (possibly crystalline regions) increases near the surface of PMDA-ODA [i].
- The surface roughness of various spin-coated and cast polyimide films have been measured for the first time [iii]. Spin-coated films are smoother.
- A composite film of PTFE and SiO_2 particles (Rogers 2800) has lower surface energy over the particles even though XPS indicates that the particles are covered by a thin film of PTFE [manuscript in preparation].
- A major review of metal adhesion to polyimides was prepared [iv].

3. Highlights of Results on Ceramic Surfaces: The AFM has been used to examine the surface microstructure and morphology of several single crystal and thin film ceramic materials. Major results include:

- The stability and microstructure of single crystal TiO_2 low index (100), (110) and (001) surfaces was systematically studied. A wealth of experiments on these surfaces over the past decade make them a well-established model system for oxide surface studies. Using AFM the (100) and (001) surfaces were found to facet at high temperatures [x] and the defect structure of the (110) surface was shown to be processing dependent [ix].
- The surface morphology of fractured Cr_2O_3 and NiO single crystals was investigated. Single atomic height steps and kinks are present on cleaved Cr_2O_3 surfaces. NiO cleavage surfaces are rough and have no single height steps; the minimum step height is 20 Å [viii,ix].
- A regular single step - terrace structure was imaged on polished r-cut sapphire substrates [ix]. No steps are visible on similarly prepared c-axis sapphire substrates.
- SnO_2 films deposited by rf-sputter deposition on r-cut sapphire substrates grow with perfect epitaxy at 500 C. AFM imaging shows the substrate step structure persisting after deposition of a 400 Å thick film indicating that the growth occurs via a layer-by-layer mechanism controlled by diffusion of adatoms to step edges [xi].
- A monolayer of Pd deposited onto epitaxial SnO_2 films is dispersed at 300K and forms clusters after annealing to 500K in vacuum [xii].
- The amorphous to crystalline phase transition on rf-sputter deposited WO_3 films was characterized and the film microstructure was correlated with H_2S gas sensing response [xiii].
- Vanadium carbide surfaces are extremely hard and degrade the Si_3N_4 AFM tips during imaging [ix]. Epitaxial vanadium oxide crystallites grow during high temperature oxidation [manuscript in preparation].

Presentations of Research Results

1. Publications:

i. "Nanometer-Scale Modification and Imaging of Polyimide Films by Scanning Force Microscopy," W. N. Unertl and X. Jin in **Thin Films: Stresses and Mechanical Properties III**, Mater. Res. Soc. Symp. Proc. Vol. **239**, (1992) 535-540.

ii. "Submicrometer Modification of Polymer Surfaces with a Surface Force Microscope," X. Jin and W. N. Unertl, Appl. Phys. Lett. **61** (1992) 657-659.

iii. "Model Studies of the Interface Between Metals and Polyimides," W. N. Unertl and R. G. Mack in **Metallized Plastics 3: Fundamental and Applied Aspects**, Edited by K. L. Mittal (Plenum, New York, 1992) p. 85-108.

iv. "Adhesion of Metals to Polyimide," W. N. Unertl and L. J. Matienzo in **Polyimides: Fundamental Aspects and Technological Application**, Edited by M. K. Ghosh and K. L. Mittal (Marcel Dekker, New York). In preparation for publication in Fall, 1993.

v. "Atomic Force Microscopy of Polymer Surfaces", W. N. Unertl and X. Jin in **Mechanical Properties and Deformation Behavior of Materials Having Ultra-Fine Microstructures**, Eds. M. Nastasi, D. M. Parkin, and H. Gleiter (Kluwer, Dordtrecht, 1993) p. 581-586.

vi. "Force Microscopy of Clean and Gold Covered Polyimide films," W. N. Unertl, X. Jin, and R. C. White, **Polyimides and Other High-Temperature Polymers**, Eds. M. J. M. Abadie and B. Sillion (Elsevier, Amsterdam, 1991) 427-435.

vii. "Nanoscale deformations of polyimide with a force microscope," J. A. Lin and W. N. Unertl, J. Adhesion Sci. (submitted).

viii. "Imaging of Defect Microstructure at Oxide Single Crystal Surfaces by Atomic Force Microscopy," R.J. Lad and M.D. Antonik, Ceramic Transactions **24**, 359 (1991).

ix. "Faceting, Reconstruction, and Defect Microstructure at Ceramic Surfaces Revealed By Atomic Force Microscopy," M.D. Antonik and R.J. Lad, J. Vac. Sci. Technol. A **10**, 669 (1992).

x. "Facet Formation on Single Crystal TiO_2 Surfaces Studied by Atomic Force Microscopy," M.D. Antonik, J.C. Edwards, and R.J. Lad, Proc. Materials Research Soc. **237**, 459 (1992).

xi. "Layer-by-layer Growth of Epitaxial SnO_2 on Sapphire by Reactive Sputter Deposition," R.E. Cavicchi, S. Semancik, M.D. Antonik, and R.J. Lad, Applied Physics Letters **61**, 1921 (1992).

xii. "Structure and Morphology of Pd Overlayers on Epitaxial SnO_2 Films Studied with the Atomic Force Microscope," R.J. Lad, M.J. Matthews, M.D. Antonik, R.E. Cavicchi, and S. Semancik, Proc. Materials Research Soc. **280**, 641 (1993).

xiii. "Microstructural Effects in WO_3 Gas Sensing Films," M.D. Antonik, J.E. Schneider, E.L. Wittman, K. Snow, J.F. Vetelino, and R.J. Lad, Thin Solid Films (submitted).

2. Presentations at Seminars and Meetings:

Presentations by W.N. Unertl

i. "The Atomic Force Microscope," Physics Department Colloquium, Dartmouth College, 18 January, 1991.

ii. "Modification of Polymer Surface Structure with a Force Microscope," X. Jin, W. N. Unertl, and R. C. White, Bull. Am. Phys. Soc. 36 (1991) 889.

iii. "Atomic Force Microscopy," Featured talk at Annual Meeting of Maine Association of Physics Professors, Orono, ME , 27 April, 1991.

iv. "Force Microscopy of Clean and Gold Covered Polyimide films," W. N. Unertl, X. Jin, and R. C. White, **Proceeding of the 2nd European Technical Symposium on Polyimides and High-Temperature Polymers**, Montpellier, France, 6 June 1991.

v. "Atomic Force Microscopy of Polymers," Seminar given on 12 June 1991 at University of Heidelberg, Germany, on 20 June 1991 at Imperial College of Science and Technology, London, and on 28 June 1991 at the Liverpool University.

vi. "Model Studies of the Interface Between Metals and Polyimides," W. N. Unertl, Invited talk at 180th Electrochem. Soc. Meeting, Phoenix, 16 Oct 1991.

vii. "Nanometer Mechanics and Imaging with the Atomic Force Microscope," Colloquium, Dept. of Elec. Eng., Marquette Univ, 12, Nov 1991.

viii. "Nanometer-Scale Modification of Polyimides Using Scanning Force Microscopy," Poster at 38th Natl.Symp. of the Am. Vac. Soc., Seattle, 13 Nov 1991.

ix. "Atomic Force Microscopy at the University of Maine," Colloquium, Dept. of Chem. Eng., Univ. of Maine, 22 Nov 1991.

x. "Force Microscopy and Micromachining of Polymer Surfaces," X. Jin and W. N. Unertl, Bull. Am. Phys. Soc. 37 (1992) 727.

xi. "The Atomic Force Microscope," Physics Dept. Colloquium, Ohio University, 8 April 1992.

xii. "Applications of Atomic Force Microscopy to the Study of Polymer Surfaces", Program in Polymer Science and Technology, MIT, 5 June, 1992.

xiii. " Interfacial Adhesion Studies of Polyimides with the Scanning Force Microscope", ONR/NRL Workshop on Adhesion and Intermolecular Forces, Alexandria, VA, 18 June, 1992.

xiv. "Mechanisms of Metal Interactions with Polyimide Substrates", IBM Technology Products Technical Liaison Meeting, Endicott, NY, 22 June, 1992.

xv. "Atomic Force Microscopy of Polymer Surfaces", NATO Advanced Study Institute on Mechanical Properties and Deformation Behavior of Materials Having Ultra-Fine Microstructure, Praia do Novo Porto, Portugal, June 28-July 10, 1992.

xvi. "Does the Atomic Force Microscope Have Atomic Resolution?" Surface Science Seminar, Cornell Univ., October 7. 1992.

xvii. "Initial Stages of Cu Film Growth on Higher Performance Polyimides", W. N. Unertl, R. G. Mack, and L. J. Matienzo, 39th National Symposium of the American Vacuum Society, Nov 9-13, 1992, Chicago.

xviii. "Sub-Micrometer-Machining of Polyimide Surfaces with and Atomic Froce Microscope", X. Jin and W. N. Unertl, 39th National Symposium of the American Vacuum Society, Nov 9-13, 1992, Chicago.

xix. "Groove Fabrication on Polyimide Surfaces with a Force Microscope and the Effect of Nonliniarity of the Tube Scanner," J. A. Lin and W. N. Unertl, Bull. Am. Phys. Soc. 38 (1993) 378.

xx. "A Force Microscope for Ultra High Vacuum Studies of Contact Adhesion," W. N. Unertl and R. J. Lad, Bull. Am. Phys. Soc. 38 (1993) 379.

xxi. "Wetting Behavior of Latex Spheres on Heated Mica Substrates," W. J. Kulnis, Jr. and W. N. Unertl, Bull. Am. Phys. Soc. 38 (1993) 543.

Presentations by R.J. Lad

xxii. "Microstructure of Single Crystal Oxide Surfaces Studied by Atomic Force Microscopy," Scanning Probe Microscopy Conference, Rutgers University, Piscataway, NJ, November 1990. (Poster).

xxiii. "Atomic Force Microscope Studies of Ceramic Materials," Department of Physics & Astronomy Colloquium, University of Maine, Orono, ME, February 1991.

xxiv. "Morphology and Structure of Fractured Cr_2O_3 $(10\bar{1}2)$ and NiO (100) Surfaces Imaged by Atomic Force Microscopy," Meeting of the American Physical Society, Cincinnati, OH, March 1991.

xxv. "Defect Microstructure of Oxide Surfaces Imaged by Atomic Force Microscopy," American Ceramic Society Symposium on Point Defects and Related Properties of Ceramics, Cincinnati, OH, April 1991.

xxvi. "Faceting, Reconstruction, and Defect Microstructure at Ceramic Surfaces Revealed By Atomic Force Microscopy," American Vacuum Society 37th National Symposium, Seattle, WA, November 1991.

xxvii. "Kinetics of Facet Formation on Single Crystal TiO_2 Surfaces Studied by Atomic Force Microscopy," Fall Meeting of the Materials Research Society, Boston, MA, December 1991.

xxviii. "Electronic and Structural Properties of Ceramic Surfaces: An Overview," Department of Materials Science & Engineering Seminar, Cornell University, Ithaca, NY, March 1992.

xxix. "Atomic Force Microscope Characterization of Ceramic Surfaces," Solid State Physics Seminar, Boston University, Boston, MA, October 16, 1992 (Invited).

xxx. "Microstructural Effects in WO_3 Gas Sensing Films," American Vacuum Society 38th National Symposium, Chicago, IL, November 1992.

xxxi. "Applications and Limitations of the Atomic Force Microscope," Department of Mechanical Engineering Colloquium, University of New Hampshire, Nov. 1992.

xxxii. "Structure and Morphology of Pd Overlayers on Epitaxial SnO_2 Films Studied with the Atomic Force Microscope,"

Fall Meeting of the Materials Research Society, Boston, MA, December 1992 (Poster).

xxxiii. "Microstructural Characterization and Thermal Stability of Stoichiometric and Au-doped WO_3 Thin Films," Fall Meeting of the Materials Research Society, Boston, MA, December 1992 (Poster).

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