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W.N. Unertl

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This report summarizes research on

1. Fabrication and Processing of Polyimide Thin Films
2. Mechanical Modification of Polyimide surfaces
3. Polyimide-on-metal adhesion
4. Metal-on-polyimide adhesion

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OFFICE OF NAVAL RESEARCH

FINAL REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

ONR Grant No: N00014-89-J-1314

R&T Code 413e019

OVERLAYER ADHESION AND PASSIVATION OF ELECTRONIC MATERIALS

W. N. Unertl
M. Grunze
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16 July 1992

OFFICE OF NAVAL RESEARCH

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 413E019---05

Grant Number: N00014-89-J-1314

Grant Title: **Overlayer Adhesion and Passivation of Electronic Materials**

Principal Investigator: William N. Unertl
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E-Mail Address: None

a. Number of papers submitted to refereed journals but not published: 5

b. Number of papers published in refereed journals (list attached): 11

c. Number of books or chapters submitted, but not yet published: 0

d. Number of books or chapters published (list attached): 7

e. Number of printed technical reports & non-refereed papers (list attached): 18

f. Number of patents filed: 0

g. Number of patents granted: 0

h. Number of invited presentations at workshops and professional society meetings: 19

i. Number of presentations at workshops and professional society meetings: 18

j. Honors/Awards/Prizes for contract/grant employees(list attached): 1

k. Total Number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period, under this R&T project number:

Graduate Students: 5

Post-Doctoral Associates: 1

including the number of,

Female Graduate Students: 0

Female Post-Doctoral Associates: 0

the number of

Minority Graduate Students: 0

Minority Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students: 1

Asian Post-Doctoral Associates: 0

l. Other Funding (list attached)

a. Papers Submitted to Refereed Journals

1. "Mechanism of X-ray Induced Degradation of Pyromellitic Dianhydride," T. Strunskus, C. Hahn and M. Grunze, submitted to J. Electron. Spectrosc. (1992).
2. "Effect of Excess Oxydianilene on the Properties of Polyimide," R. G. Pethe, W. N. Unertl, and C. M. Carlin, J. Polymer Sci.:Polymer Lett. submitted.
3. "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. Proc. **130**, Pittsburg, PA, 1992) in press.
4. "Sub-micrometer Modification of Polymer Surfaces with a Surface Force Microscope," X. Jin and W. N. Unertl, Appl. Phys. Lett. (to appear Aug, 1992).
5. "Model Studies of the Interface Between Metals and Polyimides," W. N. Unertl, J. Electrochem. (1992) (in press).

b. Published Papers in Refereed Journals:

1. "Adhesion of Vapor Phase Deposited Ultrathin Polyimide Films on Polycrystalline Silver," M. Grunze and R.N. Lamb, Surface Science, **204** (1988) 183; supported in part by the Royal Society and an NSF Instrumentation Grant DMR 84-03831.
2. "Chemistry of Adhesion at the Polyimide-Metal Interface," M. Grunze, W.N. Unertl, S. Gnanarajan and J. French, Materials Research Society Symposium Proceedings Vol. **108** (1988) 189.
3. "A Raman Spectroscopic Study of Vapor Deposited Poly[N,N'-bis(phenoxyphenyl)pyromellitimide] Films," R. G. Mack, H.H. Patterson, M.R. Cook and C.M. Carlin, J. Polymer Sci. **27** (1989) 25.
4. "Chemical Cleaning of Metal Surfaces in Vacuum Systems by Exposure to Reactive Gases," M. Grunze, H. Ruppender and O. Elshazly, J. Vac. Sci. Technol. **A6** (1988) 1266; supported in part by NSF Grant DMR 84-03831 and DOE Grant DE-FG22-85PC80515.
5. "The Interaction of the Polyimide Precursors PMDA and m-PDA with Ni(110)," T. S. Jones, M. R. Ashton, N. V. Richardson, R. G. Mack, and W. N. Unertl, J. Vac. Sci. Technol. **A8** (1990) 2370.
6. "Interaction of Copper with a Vapor Deposited Polyimide Film," R. G. Mack, E. Grossman, and W. N. Unertl, J. Vac. Sci. Technol. **A8** (1990) 3827.
7. "Interfacial Chemistry of Titanium Films Deposited on PMDA-ODA Polyimides," W. N. Unertl, High Performance Polymers **2** (1990) 15.
8. "The Chemistry of Polyimide Precursors and Related Molecules on Metal Surfaces," M. R. Ashton, T. S. Jones, N. V. Richardson, R. G. Mack, and W. N. Unertl, J. Electr. Spectr. **54/55** (1990) 1133.
9. "FTIRAS Study of Vapor Deposited Pyromellitic Dianhydride and Oxydianiline and their Solid-State Reaction to Polyimide on Pt(111)," C. Hahn, T. Strunskus, D. Frankel, and M. Grunze, J. Electr. Spectr. **54/55** (1990) 1123.
10. "Interaction of Evaporated Copper with Vapor Deposited Thin Polyimide Films," T. Strunskus, C. Hahn, D. Frankel and M. Grunze, J. Vac Sci. Technol. **A9**(3) (1991) 1272.
11. "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.

d. Books or Chapters published:

1. "Solventless Polyamic Acid: Consequences for Reactivity with Metals," T. Strunskus, M. Grunze, and S. Gnanarajan, Chapter 26 in *Metallization of Polymers*, Eds. E. Sacher, J. J. Pireaux, and S. P. Kowalczyk (Am. Chem. Soc. 1990) p. 353-369.

2. "Properties and Adhesion of Polyimides in Microelectronic Devices," M. Grunze in *Advanced Materials and Processes*, Eds: H. E. Exner and V. Schumacher, Proceedings of EUROMAT '89 European Conference on Advanced Materials and Processes, November 22-24, 1989, Aachen (FRG), Vol. 2 (1990), p. 871-880.

3. "Chemische Bindung und Orientierung von Makromolekülen auf Oberflächen," M. Grunze, G. Hähner, M. Kinzler, C. Mainka, W. Meyer, A. Ortega-Villamil, Ch. Wöll und W. Schrepp, in *Berichtsbandzum Symposium Haftung bei Verbundwerkstoffen und Werstoffverbunden*, (W. Brockmann, Konstanz, 1990) p. 11-31.

4. "Vapor Deposition of Polyimide Precursors on Copper," R.N. Lamb, M. Grunze, J. Baxter, C.W. Kong and W.N. Unertl, in *Adhesion and Friction*, Eds. M. Grunze and H.J. Kreuzer (Springer Verlag, Berlin, 1989) p. 36-52.

5. "Chemical and Structural Studies of Polyimide/Metal Interfaces" in **Handbook of Polymer Metallization**, M. Grunze and T. Strunskus, ed. S.P. Kowalczyk, Marcel Dekker, New York, in press.

6. "Comparison Between the Interfacial Chemistry of Metallized Polyimides and Polyimide Films on Bulk Metal Substrates," M. Grunze, A. Killinger, C. Mainka, C. Hahn, T. Strunskus, Proceedings of the 2nd Symposium on Metallized Plastics Fundamental and Applied Aspects, Electrochemical Society Meeting in Montreal, May 1990, ed. K.L. Mittal, (1991) 165-177.

7. "Surface Structure," Chapter Five in a textbook, **Scanning Tunneling Microscopy: Theory and Application**, Ed. D. A. Bonnell (VCH Publishers, New York, 1991).

e. Printed technical reports & non-refereed papers :

1. M. Grunze and R.N. Lamb, "Chemistry of Adhesion at the Polyimide/Metal Interface," Fourth Symposium on Surface Science, Austria, 1989.

2. ONR Technical Report No. 1: R.G. Mack, H. H. Patterson, M. R. Cook and C.M. Carlin, "A Raman Spectroscopic Study of Vapor Deposited Poly[N,N'-bis(phenoxyphenyl)pyromellitimide] Films," Jour. of Polymer Sci. Vol. 27 (1989) 25-32; this work was supported by the Office of Naval Research.

3. ONR Technical Report No. 2: M. Grunze and R.N. Lamb, "Adhesion of Vapour Phase Deposited Ultra-Thin Polyimide Films on Polycrystalline Silver," Surf. Sci. 204 (1988) 182-212; this work was supported by the Office of Naval Research; National Science Foundation Grant No. DMR-8403831, and the Royal Society.

4. ONR Technical Report No. 3: M. Grunze, W.N. Unertl, S. Gnanarajan and J. French, "Chemistry of Adhesion at the Polyimide-Metal Interface," Mat. Res. Soc. Symp. Proc., Vol. 108, pp. 189-199, 1988 Materials Research Society; this work was supported by the Office of Naval Research.

5. ONR Technical Report No. 4: T.S. Jones, M.R. Ashton, N.V. Richardson and W.N. Unertl, "The Bonding of Polyimide Precursors to Ni Studied by Electron Energy Loss Spectroscopy," J. Condensed Matter, 1989, (in press); this work was supported by the Office of Naval Research; Courtaulds Coatings, U.K., and by a NATO travel grant.

6. ONR Technical Report No. 5: T.S. Jones, M.R. Ashton, N.V. Richardson, R. G. Mack and W.N. Unertl, "The Interaction of the Polyimide Precursors PMDA and m-PDA with Ni(110)," J.

Vac. Sci. Technol., 1989, submitted; this work was supported by the Office of Naval Research; Courtaulds Coatings, U.K., and by a NATO travel grant.

7. ONR Technical Report No. N00014-89-J-1314-6: R. G. Mack, E. Grossman, and W. N. Unertl, "Interaction of Copper with a Vapor Deposited Polyimide Film," Manuscript submitted to J. Vac. Sci. Technol. **A8** (1990) in press. This work was supported by ONR and IBM.

8. ONR Technical Report No. N00014-89-J-1314-7: W. N. Unertl, "Interfacial Chemistry of Titanium Films Deposited on PMDA-ODA Polyimides," Manuscript submitted to High Performance Polymers, 1990. This work supported by ONR and IBM.

9. ONR Technical Report No. N00014-89-J-1314-8: T. Strunskus, M. Grunze, and S. Gnanarajan, "A Model for Solventless PMDA/ODA Polyamic Acid: Consequences for the Reactivity of Polyamic Acid with Metals," Manuscript submitted for **Proceedings of the International Symposium on Metallization of Polymers**, Montreal, 1989, in press. This work supported by ONR.

10. ONR Technical Report No. N00014-89-J-1314-9: M. Grunze, "Properties and Adhesion of Polyimides in Microelectronic Devices," Manuscript submitted for **Proceedings of EUROMAT '89 European Conference on Advanced Materials and Processes**, November, 1989, Aachen, in press. This work supported by ONR.

11. ONR Technical Report No. N00014-89-J-1314-10: R. N. Lamb, M. Grunze, J. Baxter, C. W. Kong, and W. N. Unertl, "Vapor Deposition of Polyimide and Polyimide Precursors on Copper," Manuscript submitted for **Adhesion and Friction,** Eds. M. Grunze and H. J. Kreuzer (Springer Verlag, Berlin, 1989) p. 36-52. This work supported by ONR.

12. ONR Technical Report No. N00014-89-J-1314-11: M. R. Ashton, T. S. Jones, N. V. Richardson, R. G. Mack, and W. N. Unertl, "The Chemistry of Polyimide Precursors and Related Molecules on Metal Surfaces." Reprint of paper published in J. Electron Spectroscopy and Related Phenomena **54/55** (1990) 1133. Work supported by ONR and NATO.

13. ONR Technical Report No. N00014-89-J-1314-12: R. G. Pethe, W. N. Unertl, and C. M. Carlin, "Effect of Excess Oxydianiline on the Properties of Polyimide," preprint of paper submitted to J. Polymer Sci. Work supported by ONR

14. ONR Technical Report No. N00014-89-J-1314-13: W. N. Unertl, "Surface Structure," Manuscript of Chapter 5 of the textbook, *Scanning Tunneling Microscopy: Theory and Application*, Ed. D. A. Bonnell. To be published by VCH Publishers, New, York (1991). Work supported by ONR and NSF.

15. ONR Technical Report No. N00014-89-J-1314-14: R. G. Pethe, W. N. Unertl, and C. M. Carlin, preprint of "Effect of Excess Oxydianiline on the Properties of Polyimide," submitted to J. Polymer Sci.: Polymer Lett. (1991). Work supported by ONR.

16. ONR Technical Report No. N00014-89-J-1314-15: C. Hahn, T. Strunskus, D. Frankel, and M. Grunze, reprint of: "FTIRAS Study of Vapor Deposited Pyromellitic Dianhydride and Oxydianiline and their Solid-State Reaction to Polyimide on Pt(111)," C. Hahn, T. Strunskus, D. Frankel, and M. Grunze, J. Electr. Spectr. **54/55** (1990) 1123. Work supported by ONR, Bundesminister fur Forschung and Tecknik, and Univ. of Maine.

17. ONR Technical Report No. N00014-89-J-1314-16: T. Strunskus, C. Hahn, and D. Frankel, "Interaction of Evaporated Copper with Vapor-Deposited Thin Polyimide Films," to be published in J. Vac. Sci. Technol. Work supported by ONR, IBM and the Univ. of Maine.

18. ONR Technical Report No. N00014-89-J-1314-17: T. Strunskus, C. Hahn, D. Frankel, and M. Grunze, "Degradation of Pyromellitic Dianhydride during XPS Analysis," submitted to J. Vac. Sci. Technol. Work supported by ONR and the Univ. of Maine.

h. Invited Presentations

1. M. Grunze, "Photoemission Studies on Polymer/Metal Interfaces," Bunsencolloquium on "Technologies to Study Polymer/Metal Interfaces," April 17-18, 1989, BASF, Ludwigshafen, West Germany.
2. W.N. Unertl, "Early Stages of Metal Growth on Polymers by Tunneling Microscopy and XPS," Topical Conference on the Sciences of Electronic Packaging, IBM, Endicott, NY, May 2-3, 1989.
3. W. N. Unertl, "Early Stages of Metal Growth on Polymers by Tunneling Microscopy and XPS, " Topical Conf. on Sciences of Electronic Packaging, IBM, Endicott, NY, May, 1989.
4. M. Grunze, Comparison Between the Interfacial Chemistry of Metallized Polyimides and Polyimide Films on Bulk Metal Substrates". 177th Meeting of the Electrochemical Society, Montreal, May 6-11, 1990.
5. M. Grunze, "Properties and Adhesion of Polyimides in Microelectronic Devices," EUROMAT '89 European Conference on Advanced Materials and Processes, November, 1989, Aachen.
6. M. Grunze, "A Model for Solventless PMDA/ODA Polyamic Acid: Consequences for the Reactivity of Polyamic Acid with Metals," International Symposium on Metallization of Polymers, Montreal, May, 1989.
7. M. Grunze, "Bonding and Orientation in Polymer/Metal Interfaces," The Adhesion 14th Annual Meeting in Clearwater, Florida, February 1991.
8. T. Strunskus, "Metallization of Polyimides Revisited: What Can We Learn from Infrared Reflection Absorption Spectroscopy?" 181st Meeting of the Electrochemical Society, Phoenix, AZ, October, 1991.
9. W.N. Unertl, "Metal Interactions with Polyimides," Surface Science Research Center, Liverpool University, Liverpool, England, June, 1990.
10. W.N. Unertl, "Properties of the Metal Polyimide Interface," IBM T. J. Watson Research Center, Yorktown Heights, NY, July, 1990, and Surface/Interface Seminar Series, Columbia University, October, 1990.
11. W.N. Unertl, "The Atomic Force Microscope," Physics Department Colloquium, Dartmouth College, 18 January, 1991.
12. W.N. Unertl, "Atomic Force Microscopy," Featured talk at Annual Meeting of Maine Association of Physics Professors, Orono, ME , 27 April, 1991.
13. W.N. Unertl, "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.
14. W.N. Unertl, "Model Studies of the Interface Between Metals and Polyimides," Invited talk at 180th Electrochem. Soc. Meeting, Phoenix, 16 Oct 1991.
15. W.N. Unertl, "Nanometer Mechanics and Imaging with the Atomic Force Microscope," Colloquium, Dept. of Elec. Eng., Marquette Univ, 12, Nov 1991.
16. W.N. Unertl, "Atomic Force Microscopy at the University of Maine," Colloquium, Dept. of Chem. Eng., Univ. of Maine, 22 Nov 1991.

17. W.N. Unertl, "The Atomic Force Microscope," Physics Dept. Colloquium, Ohio University, 8 April 1992.

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

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

i. Contributed Presentations at Topical or Scientific/Technical Society Conferences:

1. T. Strunskus, R. G. Mack, M. Grunze and W.N. Unertl, "Interaction of PMDA-ODA Polyimide with $YBa_2Cu_3O_{7-x}$," American Physical Society, St. Louis, 20-24 March 1989.
2. W.N. Unertl, "Adhesion at the Polyimide-Metal Interface," Seminar at GA Technologies, San Diego, March 1989.
3. T. S. Jones, M. R. Ashton, N. V. Richardson, R. G. Mack, and W. N. Unertl, "The Interaction of the Polyimide Precursors PMDA and m-PDA with Ni(110)", AVS Nat'l Symp, Boston, Oct, 1989. Supported in part by a NATO travel grant.
4. R. G. Mack, E. Grossman, and W. N. Unertl, "Interaction of Copper with a Vapor Deposited Polyimide Film", AVS Nat'l Symp, Boston, Oct, 1989.
5. W. N. Unertl, "Interfacial Chemistry of Titanium Films Deposited on PMDA-ODA Polyimides", American Chemical Society Symposium on Recent Advances in Polyimides and Other High Performance Polymers, San Diego, January, 1990.
6. T. Strunskus, C. Hahn, D. Frankel and M. Grunze, "Interaction of Evaporated Copper with Vapor Deposited Thin Polyimide Films," AVS National Symposium, Toronto, Oct. 1990.
7. C. Hahn, T. Strunskus and M. Grunze, "Structural Phase Transition in Adsorbate Phases of Pyromellitic Dianhydride and 4,4'-Oxidianiline," AVS National Symposium, Seattle, Nov. 1991.
8. T. Strunskus, C. Hahn and M. Grunze, "Chromium on Polyimide Revisited: What Can We Learn from Infrared Reflection Absorption Spectroscopy?" AVS National Symposium, Seattle, Nov. 1991.
9. "Interaction of Copper with a Vapor Deposited Polyimide Film," AVS Nat'l Symp, Boston, Oct, 1989.
10. "Force Microscopy of Clean and Gold Covered Polyimide Films," Poster presentation at Symposium on Scanning Probe Microscopy, Greater New York Chapter of the American Vacuum Society, Rutgers University, November, 1990.
11. "Solventless Deposition of Polyimides Studied by Raman Spectroscopy," R. Pethe and W. N. Unertl, Bull. Am. Phys. Soc. **36** (1991) 693.
12. "Interaction of Polyimide Precursor Molecules with Ni(110): Implications for Adhesion," R. G. Mack, W. N. Unertl, M. R. Ashton, T. S. Jones, and N. V. Richardson, Bull. Am. Phys. Soc. **36** (1991) 889.
13. "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.
14. "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.
15. "Nanometer-Scale Modification of Polyimides Using Scanning Force Microscopy," Poster at 38th Natl.Symp. of the Am. Vac. Soc., Seattle, 13 Nov 1991.

16. "Reaction of Aniline and Phenylene Diamine with Monolayer PMDA: Model for Polyimide Bonding and Adhesion," B. G. Frederick, N. V. Richardson, W. N. unertl, and A. El Farrash, Bull. Am. Phys. Soc. 37 (1992) 726.
17. "Force Microscopy and Micromachining of Polymer Surfaces," X. Jin and W. N. Unertl, Bull. Am. Phys. Soc. 37 (1992) 727.
18. "Interfacial Adhesion Studies of Polyimides with the Scanning Force Microscope", ONR/NRL Workshop on Adhesion and Intermolecular Forces, Alexandria, VA, 18 June, 1992.

j. Honors/Awards/Prizes:

1. W.N. Unertl, Visiting Fellow at the Centre for Chemical Physics, University of Western Ontario, London, Ontario, February 1-15, 1989.

k. Total Number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period, under this R&T project number:

4 graduate students 1 post-doctoral associates

l. Other Funding

Agency	Title	Total Amount	Period of Performance
NSF	Kinetics of Ordering for Surface Phase Transitions	$225,000	1 May 1988 -31 Oct 1991
NATO	Chemical Origins of Polyimide Adhesion	$5,000	1 August 1988-31 August 1991
AFOSR	Direct Imaging of the Surface Microstructure of Dielectric Materials Using an Atomic Force Microscope	$216,000	1 April 1990 -31 March 1993
IBM-Endicott	Metal Adhesion to Complex Polyimides	$61,608	1 Feb. 1990 - 31 Jan. 1991
Exxon Research & Engineering Co.	"Support for One Graduate Student	$30,000	1 Mar 1990 - 28 Feb. 1992
ONR & AFSOR	"1990 LASST-ACSIS Joint Workshop on Interface Phenomena	$15,517	1 Jan. 1990 - 1 Jan 1991
NSF	Study of a Surface Acoustic Wave Microsensor for Gas Detection	$611,897	1 May 1987 - 30 April 1990

PART II

a. Principal Investigator: William N. Unertl
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Co-investigators: Michael Grunze, Professor of Physics
David Frankel, Senior Research Scientist

b. Telephone Number: 207-581-2254

c. Cognizant ONR Scientific Officer: David Nelson and Mark Ross

d. Description of Project:

Polyimide films are important in electronic packaging and composite materials. Reliable adhesion is crucial in these applications. The purpose of this project is to determine the chemical factors which result in good adhesion between polyimide films and other materials and to determine how processing conditions influence the topography, crystallinity, and homogeneity of the thin polyimide films. The polyimide films are prepared by Langmuir-Blodgett techniques, spin-coating, and by vapor deposition of the constituent dianhydride and diamine molecules followed by in situ curing. The substrates of interest include metals, semiconductors, and ceramics. The films are characterized using atomic force microscopy, scanning tunneling microscopy, x-ray photoelectron microscopy, high resolution electron energy loss spectroscopy, Fourier transform infra red spectroscopy, Raman spectroscopy, and near edge x-ray absorption spectroscopy.

e. Significant Results

1. Fabrication and Processing of Polyimide Thin Films

a. One-to-five monolayer thick polyimide films have been fabricated by Langmuir-Blodgett techniques on gold and silver substrates and shown to have a higher degree of ordering but lower thermal stability than vapor deposited films.
b. Vapor deposition was used to fabricate ultra-thin films from PMDA and m-phenylene diamine (mPDA). This polyimide was found to have a high degree of imperfections associated with the nitrogen linkage. HREELS and XPS studies of the adsorption of the individual precursor molecules of this polyimide with the Ni(110) surface showed that chemical adhesion can occur only through terminal groups on the PMDA.
c. Co-deposition of PMDA and ODA onto Pt(111) at low temperature followed by heating was used to demonstrate that the interaction with the surface near room temperature is primarily through polyamic acid rather than PMDA or ODA.
d. Thermally unstable imine bonds were shown to cause degradation of the polyimide. Imine bonds can be formed by branching of the molecular backbone or by reaction of the polymer with excess monomers. Excess PMDA during solventless growth of PMDA-ODA films minimizes imine bond formation.
e. Both Langmuir-Blodgett and vapor deposited films with thickness greater than three layers have the polymer chains oriented parallel to the substrate surface as shown by near edge absorption fine structure measurements carried out at BESSY in Berlin. On Ag, the interfacial structure differs from that of the thicker films but is not yet understood in detail.

f. Polyimide films can be grown on high temperature superconductors if the imidization is carried out in oxygen to prevent release of atomic oxygen from the heated superconductor substrate.
g. The feasibility of studying diffusion of molecules through the polyimide using surface acoustic wave (SAW) devices with polyimide thin films on them has been demonstrated.
h. Langmuir-Blodgett deposited polyimide films were used to determine the electron attenuation length of 1150 eV electrons in polyimide to be 42 Å. This large value indicates a low packing density for these polyimide films.

2. Modification of Polyimide Surfaces

a. The first studies of polymer surfaces in air and under water with an atomic force microscope were carried out. The best resolution is about 10-20 nm in agreement with classical elasticity theory. A surprising variety of modifications is possible on these materials including: (i) scribed grooves with widths between 20 and 80 nm, (ii) raised areas with heights up to 5 nm above the original surface; and (iii) pits with depths of at least 20 nm.

3. Properties of the Polyimide-on-Metal Interface

a. The Langmuir-Blodgett technique was used to fabricate 0-25 monolayer thick polyimide films on Au and oxidized Ag and Si substrates. In the case of Si and Ag a carboxylate-like bonding is proposed between the first layer and the substrate. The interaction on Au is not yet understood but closure of the imide ring is prevented. Subsequent layers on Ag and Au are fully imidized whereas, on Si, the first three layers are influenced by the substrate and the degree of Si oxidation is increased.
b. Adsorption of a variety of polyimide precursor molecules on Ni(110) and Cu(110) surfaces was studied. The phenylenediamine molecule was shown to bond through one of its nitrogen atoms with the aromatic ring is nearly parallel to the surface. PMDA molecules bond to Ni(110) surfaces through a carboxylate-like bond and the molecules stand vertical to the surface.
c. Measurements on thin films of pure PMDA and ODA deposited onto a Pt(111) surface have revealed the presence of an amorphous-to-crystalline phase transition. Films deposited at low temperature are annealed to higher temperatures. The possibility of epitaxial growth of the crystalline phase on annealed films has been studied.

4. Properties of the Metal-on-Polyimide Interface

a. A new model was developed to explain the nature of the interaction between Cu and polyimide. Cu atoms or clusters in the vicinity of carbonyl groups cause a strong electromagnetic depolarization of the dynamic dipole moment of the carbonyl. XPS and FTIR measurements of polyimide films exposed to copper are consistent with this model as well as an alternative model in which the rupture of bonds in the imide rings is catalyzed by the copper atoms.
b. The interaction of titanium with PMDA-ODA polyimide was shown to be significantly stronger than previously reported. Ti attacks polyimide at both carbonyl sites and nitrogen sites forming an interfacial layer of mixed carbides, nitrides and oxides.
c. Changing the electron withdrawing power of the dianhydride part of the polyimide molecule was shown by XPS to have only a small effect on its interaction with Cu.

g. Names of Graduate Students and Post-Doctoral Associates on Project:

Timothy S. Jones, Rajiv Pethe, Thomas Strunskus, Melany Ashton

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SURFACE AND INTERFACE STRUCTURE OF POLYMER FILMS

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Major Goals of Research

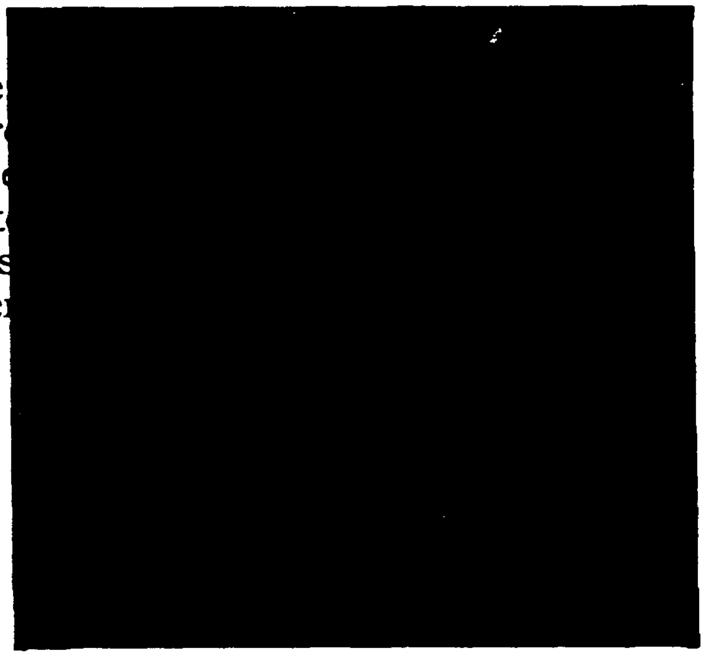
Develop molecular models of the chemical mechanisms that control polymer adhesion to other materials:

- Characterize the molecular interactions at the polymer-metal and metal-polymer interface.
- Determine the orientation of macromolecules at the interface.
- Characterize the important processing parameters that control nucleation and growth of thin metal films on polymers.

DURING THE PAST YEAR, HIGHLY ORIENTED THIN FILMS OF POLYIMIDE HAVE BEEN FABRICATED USING LANGMUIR-BLODGETT TECHNIQUES

HIGHLY ORIENTED POLYIMIDE FILMS

1) Langmuir-Blodgett technique
Monolayers of polyamic acid ar
transferred from a water surfac
onto Ag, Au, or Si(100) substrat
Multiple transfers have been us
to make films up to 5 monolaye
thick.



2) Mono- and multilayer films are cured in vacuum, nitrogen, or air t
polyimide.

3) The polymer chain orientation is determined by near-edge x-ray ab
structure (NEXAFS) through variation of the angle between the film an
polarization vector of the light. The stoichiometry of the film and its ir
the substrate is followed by x-ray photoelectron spectroscopy (XPS). P
analysis shows that the polymer chains are parallel to the surface and
degree of crystalline order.

4) In future measurements, the oriented films will be used as substra
metal deposition.

NEAR EDGE X-RAY ABSORPTION FINE STRUCTURE DATA FROM THE CARBON 1s LEVEL OF A 5 MONOLAYER POLYIMIDE FILM AS A FUNCTION OF ANGLE OF INCIDENC

Photon Energy (eV)

Absorption (Arbitrary Units)

NARRATIVE

We are studying the polymer-metal interface to determine the chemistry and physics of adhesion and the thermal and electrical properties of ultra-thin organic films. The polyimides are used as a model system because of their importance in electronic packaging applications.

Polymer surfaces and interfaces have a high degree of molecular disorder. This disorder is a major obstacle for the characterization of polymer surfaces and interfaces. Therefore, we have recently developed a Langmuir-Blodgett fabrication technique to make films of PMDA-ODA polyimide that have a very high degree of molecular order. In this technique, monolayer thick films of a polyamic acid precursor are formed on the surface of water. These films are then transferred to the surface of the substrate by passing the substrate through the film while keeping the surface tension constant. Each pass adds one monolayer.

So far, we have fabricated films with thicknesses of 1, 3, and 5 layers from both the octa-decyl ester and the octa-decyl ammonium salt of polyamic acid followed by curing in nitrogen. Ag, Si(100), and Au substrates were used. Preliminary analysis of near edge x-ray absorption fine structure (NEXAFS) data indicates a high degree of molecular order and that the polymer chains are parallel to the surface. In NEXAFS, the optical absorption near the C 1s level is measured as a function of the angle between the polarization vector of the light and the film surface. If a particular molecular orbital has a specific orientation, its absorption changes with this angle. The vu-graph shows sample NEXAFS data in which the changes in relative intensities of the various peaks demonstrate that the Langmuir-Blodgett films are oriented. Detailed quantitative analysis is in progress.

Future studies will used the ordered substrates to study metal deposition and the early stages of interface formation.

SCANNING FORCE MICROSCOPY OF POLYIMIDE FILMS

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Research Goal: Study the surface properties of polymers using Scanning Force Microscopy (SFM).

SFM controls the force between a sharp tip (radius < 400 Å) and a surface and can be used for:

1. Localized measurements of adhesion, friction, and wear.

2. Imaging surface morphology at nanometer scale resolution.

3. Nanometer scale machining of surfaces.

The Figure shows an example of machining and imaging of a BPDA-PDA polyimide surface.

SFM measurements can be carried out at the

- Air-polymer interface

- Liquid-polymer interface

No special sample preparation is required for SFM unlike other surface characterization techniques such as electron microscopy or electron spectroscopy.

Micromachined 2 x 2 μm^2 Pit on BPDA-PDA Polyimide

Load ♠ 800 nN at 0.4 μm/s

Top View of Pit

Bottom of Pit
1.5 x 1.5 μm^2

Outside of Pit
1.5 x 1.5 μm^2

A surprising variety of surface modifications are possible with SFM:

(i) Scribed grooves with widths between 20 and 80 nm. Scribing can be used for pattern generation and microsurgery.

(ii) Raised areas with heights up to 5 nm above the original surface;

(iii) Pits with depths of at least 20 nm. A 6 nm deep pit is shown in the Figure.

Modifications depend on both sample material and history. The mechanisms are under current investigation.

A single monolayer of Au is sufficient to prevent these surface modifications.

Explanatory Text:

The Scanning Force Microscope (SFM) offers a new method to measure the properties of non-conducting materials with nano-meter scale resolution.

We use the SFM to study the mechanical and adhesive properties of polymer surfaces and the effect of processing on these properties. Images of the intrinsic surface structures have been obtained for many polymeric materials and provide new, detailed views of the surprisingly wide variety of features that occur on these materials. In all cases the best resolution so far has been about 10 nm and is close to that predicted by classical elasticity theory. Resolution appears to be limited by the adhesive interaction between the SFM tip and the polymer.

The figure shows an example of a surface pit created by loading the tip to 800 nano-Newtons and raster scanning it over a 2 x 2 μm^2 area on the BPDA-PDA surface. On other materials, similar conditions result in raised areas rather than pits. The mean depth of the pit is about 6 nm and the bottom is substantially rougher than the starting surface. Polyimides are non-homogeneous near the surface because of the large number of small crystalline regions separated by more amorphous material. On PMDA-ODA the crystallites are about 150 Å in diameter. When the SFM tip cuts through the heterogeneous region it meets less resistance between the crystallites because of the lower molecular packing density there. Thus each bump in the figure can be associated with a crystallite. If the crystallite diameter is assumed to be the same as for PMDA-ODA, the volume fraction of crystallized polymer is about 15%.

A single monolayer of gold alters the surface so that surface modifications like that in the figure are no longer possible.

Commercial microfabricated cantilevers with integral Si_3N_4 tips were used; some of the tips were also coated with about 10 nm of Au. Tip radii were less than 40 nm. Surface modifications were carried out in air and at the water-polymer interface by varying the applied load (0 - 800 nN) and the speed at which the tip is drawn over the substrate (0-60 μm/s).