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POLYMER RESIST SYSTEMS FOR ADVANCED MICROLITHOGRAPHY

by

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Covering the period of June 1, 1985 through December 31, 1991

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The aim throughout this work has been to produce and characterize resist systems with enhanced sensitivity, resolution, and etch resistance. New polymers and polymer systems were evaluated as e-beam and x-ray resists using gamma radiation, flood exposure to electrons, synchrotron radiation, and e-beam patterning. The systems investigated have included copolymers and blends. In particular, reactive plasticizers were found to impart high sensitivity to negative-working resists with good resolution. Because of the overwhelming importance of the development step in producing high resolution patterns, dissolution rate measurements were refined and applied to a number of problems. As far as resistance to ion-assisted plasma etching is concerned, our studies have established the importance of conditions including flow rates, power density, pressure, etc.

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Final Report

POLYMER RESIST SYSTEMS FOR ADVANCED MICROLITHOGRAPHY

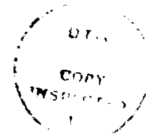
F. Rodriguez and S. K. Obendorf, Cornell University

The key to maskless pattern transfer for submicrometer geometries has been e-beam lithography. Economic use of the patterning tool demands high sensitivity resist materials. Resolution requires efficient development of the exposed pattern. The developed pattern must resist dry etching. The point of departure for most workers for many years has been high-molecular-weight poly(methyl methacrylate), PMMA. The aim throughout this work has been to produce and characterize systems with enhanced sensitivity, resolution, and etch resistance without losing the inherent advantages of adhesion, durability, reproducibility, and versatility which is typical of PMMA.

From the beginning of the project, new polymers and polymer systems were evaluated as e-beam and x-ray resists using gamma radiation, flood exposure to electrons, synchrotron radiation, and e-beam patterning (2-4, 13, 16)*. Measurements of molecular weight distribution, dissolution rates, and contrast curves were used as criteria in evaluatng these novel materials. Supplementing these measurements later on was a new and novel method of establishing the glass transition temperature using a microindenter (19).

The systems investigated have included copolymers and blends. In particular, reactive plasticizers were found to impart high sensitivity to negative-working resists with good resolution (7, 12). One of the most recent studies examined the kinetics of the deprotection step in an e-beam exposed polymer which undergoes selective loss of a t-butoxycarbonyl group (21).

Because of the overwhelming importance of the development step in producing high resolution patterns, dissolution rate measurements were refined and applied to a number of problems including the selection of solvents and the micromechanics of the dissolution process itself (1, 5, 6, 8, 9, 15, 20, 23).



The resist layer in a microlithographic scheme must, as its very name implies, "resist" the action of aggresive reagents. In particular, the ion-assisted plasma environment, usually termed "reactive ion etching (RIE)", is of interest. Organic polymers show only a modest range of resistance to the oxygen and fluoride/oxygen plasmas commonly encountered. Our studies have established the importance of conditions including flow rates, power density, pressure, etc. (10, 14, 17, 18, 22). In order to have a high degree of resistance to a plasmas, inorganic atoms need to be included in the structure (11).

*The numbers in parentheses refer to the Technical Reports listed below.

A-1

Personnel associated with the project for various periods over the six years:

Staff:

Ferdinand Rodriguez, Professor, Principal Investigator
S. Kay Obendorf, Professor, Co-Principal Investigator
Yarrow M. N. Namaste, Research Support Specialist
Camille Solbrig, Research Support Specialist
Philip Krasicky, (Post-doctoral) Research Associate
Treva Long, (Post-doctoral) Research Associate

Students significantly supported by ONR:

James Jubinsky, MS, Chemical Engineering, 1987. [Now with IBM]
Robert J. Groele, PhD, Chemical Engineering, 1988. [Now with Amoco Chemical]
Sandeep Malhotra, MS, Chemical Engineering, 1989. [Now with Motorola]
Bernard C. Dems, PhD, Chemical Engineering, 1990. [Now with Dow Chemical Co.]
Cheng-Pei Lei, MS, Fiber Science, 1992. PhD candidate, continuing at Cornell.
Ashwin Ramachandran, Chemical Engineering, MS/PhD candidate, continuing at Cornell.

Students who worked on the ONR project for only part of their time at Cornell:

Siddhartha Das, PhD, Chemical Engineering, 1986. [Now with Intel]
Leland M. Vane, PhD, Chemical Engineering, 1992. [Now with the Environmental Protection Agency.]

The following undergraduate students in chemical engineering conducted research in connection with the ONR project. Many of them became co-authors on our publications.

George Gifford, BS (ChE) '85; MEng (MatSci) '86 [Now with IBM]
David Rosenthal, BS (ChE) '86 [Now with IBM]
Sung-Won Chun, BS (ChE) '87 [Now with duPont]
Jennifer Sullivan, BS (ChE) '87 [Now with ICI America]
Jeffrey Rosenblum, BS (ChE) '87
Aaron Krasnopoler, BS (ChE) '88
Shahnaz Joarder, BS (ChE) '88 [Now with Intel]
Lisa Skeete, BS (ChE) '89
Dawn Summers, BS (ChE) '90
Brian Hand, BS (ChE) '91

The ONR-sponsored work also has led to the incorporation of several experiments into the Polymer Laboratory Course which is taken by students from various fields. Students from chemical, mechanical, materials and mechanical engineering and from fiber science usually are enrolled. The dissolution rate measurement using the laser interferometer and the glass transition characterization using the microindenter owe their incorporation into the laboratory course to the fact that ONR-sponsored research work was going on in our adjacent laboratories.

Technical Reports (with date of submission and with notation of other publication. All were presented at national meetings of ACS, AIChE, SPIE, SPE, and other organizations)

1. September 5, 1985
Krasicky, P. D., R. J. Groele, J. A. Jubinsky, F. Rodriguez, Y. M. N. Namaste, and S. K. Obendorf, "Studies of Dissolution Phenomena in Microlithography", **Polymer Eng. & Sci., 27,** 282 (1987).

2. February 28, 1986
Namaste, Y. M. N., S. K. Obendorf, and F. Rodriguez, "Methacrylamide Copolymer Resists for Electron Beam Lithography," **SPIE Vol. 631 Advances in Resist Technology and Processing** (1986), p. 91.

3. September 26, 1986
Jubinsky, J. A., R. J. Groele, F. Rodriguez, Y. M. N. Namaste, and S. K. Obendorf, "Sensitivity of Polymer Blends to Synchrotron Radiation," **Proc. ACS Div. Polym. Matls.:Sci.&Eng., 55** 125 (1986); Also in **Polymers for High Technology**, M. J. Bowden and S. R. Turner, eds, ACS Symp. Series **346**, 1987, p. 150.

4. April 17, 1987
Namaste, Y. M. N., S. K. Obendorf, J. M. Rosenblum, G. G. Gifford, R. J. Groele, B. C. Dems, and F. Rodriguez, "Lithographic Evaluation of Copolymers with Enhanced Dry Etch Resistance," **SPIE Vol. 771 Advances in Resist Technology and Processing** (1987), p. 254.

5. May 29, 1987
Krasicky, P. D., R. J. Groele, and F. Rodriguez, "Measuring and Modelling the Transition Layer during the Dissolution of Glassy Polymer Films," AIChE Meeting, Boston, August 24-27, 1986; **J. Appl. Polym. Sci., 35,** 641 (1988).

6. July 24, 1987
Rosenthal, D., R. J. Groele, F. Rodriguez, Y. M. N. Namaste, and S. K. Obendorf, "Choosing Polymer Solvents for Microlithography," presented at Conf. on Emerging Technologies, AIChE, Minneapolis, Aug. 18-20, 1987.

7. May 16, 1988
Namaste, Y. M. N., S. K. Obendorf, and F. Rodriguez, "Reactive Plasticizers in Negative E-Beam Resists," **J. Vac. Sci. Technol. B 6** (6), 2245 (1988).

8. May 16, 1988
Groele, R. J., and F. Rodriguez, "Dissolution Rates of Polymers and Copolymers Based on Methyl, Ethyl, and Butyl Methacrylate," **Proc. ACS Div. Polym. Matls.:Sci.&Eng., 59,** 1139 (1988); Also in **J. Coatings Tech., 61(774),** 55 (1989).

9. May 12, 1989
Groele, R. J., P. D. Krasicky, S-W. Chun, J. Sullivan, and F. Rodriguez, "Dissolution Rates of Poly(methyl methacrylate) in Mixtures of Non-Solvents," **J. Appl. Polym. Sci., 42,** 3 (1991).

10. May 12, 1989
Dems, B. C., F. Rodriguez, C. M. Solbrig, Y. M. N. Namaste, and S. K. Obendorf, "Reactive Ion Etching of Polymer Films," **Int. Polym. Processing, 4,** 183 (1989).

11. May 12, 1989
Namaste, Y. M. N., B. C. Dems, S. Malhotra, L. M. Vane, S. K. Obendorf, and F. Rodriguez, "Multicomponent E-Beam Resists Containing Organometallic Compounds and Reactive Monomers," **Technical Papers, RETEC**, Soc. Plastics Engs., Ellenville, 1988, pp. 157-167.

12. May 12, 1989
Namaste, Y. M. N., S. K. Obendorf, B. C. Dems, and F. Rodriguez, "Negative-Working Electron Beam Resists Based on Poly(methyl methacrylate),"**SPIE Vol. 1089 Electron-Beam, X-Ray, and Ion-Beam Technology: Submicrometer Lithographies VIII,** A. W. Yanof (ed), pp. 339-347 (1989).

13. May 12, 1989
Rodriguez, F., B. C. Dems, A. A. Krasnopoler, Y. M. N. Namaste, and S. K. Obendorf, "Molecular Weight Dependence of E-Beam Resist Sensitivity," **Proc. ACS Div. Polym. Matls.:Sci.&Eng., 60,** 458 (1989), Also in **Radiation Curing of Polymeric Materials**, C. E. Hoyle and J. F. Kinstle (eds), ACS Symp. Series. 417, pp. 516-533 (1990).

14. May 12, 1989
Dems, B. C., P. D. Krasicky, and F. Rodriguez, "Quantitative Analysis of a Laser Interferometer Waveforms Obtained During Oxygen Reactive-Ion Etching of Thin Polymer Films," **Proc. ACS Div. Polym. Matls.:Sci.&Eng., 60,** 394 (1989), Also in **Polymers in Microlithography**, E. Reichmanis, S. A. MacDonald, and T. Iwayanagi (eds), ACS Symp. Series 412, pp. 234-251 (1989).

15. February 15, 1990
Namaste, Y. M. N., S. Malhotra, B. C. Dems, F. Rodriguez, and S. K. Obendorf, "Swelling of Negative Resist Systems Used in E-Beam Lithography," **Chem. Eng. Comm., 98,** 47-54 (1990).

16. February 15, 1990
Malhotra, S., B. C. Dems, Y. M. N. Namaste, F. Rodriguez, and S. K. Obendorf, "Modified Maleic Anhydride Copolymers for Use as E-Beam Resists," "**SPIE Vol. 1263 Electron-Beam, X-Ray, and Ion-Beam Technology: Submicrometer Lithographies IX,** pp. 187-198 (1990).

17. May 7, 1990
Dems, B. C., and F. Rodriguez, "The Role of Heat Transfer During Reactive-Ion Etching of Polymer Films," **J. Vac. Sci. Technol. B 8** (6), 1985 (1990).

18. May 7, 1990
Dems, B. C., and F. Rodriguez, "Determination of Ion Power Density During Reactive-Ion Etching from Room Temperature Measurements Using Laser Interferometry," presented at AIChE meeting, San Francisco, Nov. 1989.

19. February 22, 1991
Rodriguez, F., and T. Long, "Characterization of the Glass Transition Using a Microindenter," **Proc. ACS Div. Polymer Chem., 31** (1), 268 (1990), Also to appear in **J.Appl. Polym. Sci.,**

20. February 22, 1991
Long, T., and F. Rodriguez, "Dissolution of Poly(p-hydroxystyrene): Molecular Weight Effects," **SPIE Vol. 1466 Advances in Resist Technology and Processing VIII,** pp. 188-198 (1991).

21. September 18, 1991
Long, T., S. K. Obendorf, and F. Rodriguez, "The Thermal Deprotection Process in an E-beam Exposed, Phenolic-based Polymer," **Technical Papers, RETEC**, Soc. Plastics Engs., Ellenville, 1991, pp. 281-290.

22. December 18, 1991
B. Hand, T. Long, B. C. Dems, and F. Rodriguez, "Reactive Ion Etching of Selected Polymers in O_2 and CF_4/O_2," presented at AIChE meeting, Los Angeles, Nov. 25, 1991.

23. December 18, 1991
Lei, C.-P., T. Long, S. K. Obendorf, and F. Rodriguez, "Dissolution Rates of Copolymers Based on 4-Hydroxystyrene and Styrene," submitted for presentation at ACS meeting, San Francisco, April, 1992.