The Photopolymer Science and Technology Award

The Photopolymer Science and Technology Award, No. 97300, was presented to Hiroshi Ito, Greg Breyta, Donald C. Hofer, Ratnam Sooriyakumaran, Karen Petrillo and David Seeger (International Business Machines Corporation) for their outstanding contribution published in *Journal of Photopolymer Science and Technology* 7(3), 433-448 (1994), entitled "Environmentally Stable Chemical Amplification Positive Resist: Principle, Chemistry, Contamination Resistance, and Lithographic Feasibility".

Hiroshi Ito

Hiroshi Ito is a Research Staff Member of IBM Research Division's Almaden Research Center in San Jose, California. After receiving his Ph. D. from the University of Tokyo in 1976, he worked on the synthesis of stereoregular polysaccharides for medical applications at the State University of New York in Syracuse (1976-1980) and joined IBM Research in 1980. Dr. Ito has been involved in the design and development of new advanced resist materials and is the co-inventor of chemically amplified resists. He received IBM's Outstanding Innovation Award four times and is a recipient of American Chemical Society's Doolittle Award (1989) and Cooperative Research Award (1994) and the Award of the Society of Polymer Science, Japan (1990). His research interests include preparation and evaluation of new resist materials, fundamental understanding of resist chemistry and physics, radiation chemistry and photochemistry of polymers, reactivities, kinetics, and thermodynamics in polymerization, synthesis of new polymers, and mechanistic studies of polymerization. He has more than 130 publications and more than a dozen issued patents in the field of resist materials and polymer chemistry. He is a member of the American Chemical Society, the Society of Polymer Science, Japan, and the Chemical Society of Japan.

Greg Breyta

Greg Breyta is a staff scientist at the IBM Almaden Research Center. Before joining IBM, he was involved in discovery research and later chemical scale-up in the pesticide industry. His current research interests include the scale-up and chemical process development of strategic materials used in the computer industry, along with design of new photoactive compounds for use in lithographic applications. He has a B. S. degree in Chemistry from the University of California at Berkeley.

Donald C. Hofer

Donald C. Hofer received his Ph. D. in Physical Chemistry from the University of California, Davis and has been with the Research Division of IBM since 1974. He has held a number of positions within IBM which include research staff member in x-ray lithography at the T. J. Watson Research Center, research staff member in lithography materials at the Almaden Research Center, manager, polymer materials for semiconductor packaging, Almaden Research Center, manager, thin film packaging, IBM Microelectronics Division and his present position manager, lithography, Almaden Research Center. Dr. Hofer has conducted research in a number of areas of polymer materials and processing which include high temperature polymer materials for semiconductor packaging and interconnect, naphthonovolac photoresists, 248nm chemically amplified photoresists and presently, 193nm chemically amplified photoresists. His present research interests include 248nm bilayer photoresist materials, 193nm single and bilayer photoresist materials and models for chemically amplified photoresist systems.

Dr. Hofer has pursued an active scientific and managerial career in the Research Division of IBM and has 21 patents and 119 publications in materials and processes for the semiconductor industry. He is currently a member of the American Chemical Society, Polymer Chemistry and Polymer Materials Science and Engineering Divisions and the Society for Photo Optical Instrumentation Engineers (SPIE).

Ratnam Sooriyakumaran

Ratnam Sooriyakumaran received his B.S. degree in Chemistry from the University of Sri Lanka and his Ph. D. degree in Organic Chemistry from the North Dakota State University. He joined the IBM Research Center in San Jose as a Postdoctoral Fellow in 1985 and from 1988 to 1994 he worked for IBM Microelectronics in East Fishkill. He is currently working at the IBM Almaden Research Center on the development of new photoresists.

Karen Petrillo

Karen Petrillo joined IBM in 1977 after completing a B. A. degree from the State University College at Oswego, NY. She is involved in advanced photoresist processing and material development at the T. J. Watson Research Center, Yorktown Heights, NY. In her career at IBM, she has been involved in photoresist processing for device applications at g, h, i, and deep-UV wavelengths. Karen has recently been involved in photoresist optimization for x-ray lithography, x-ray mask process development, and e-beam process development for both direct write and optical mask making applications.

David Seeger

David Seeger joined IBM in 1983 after receiving his Ph. D. in organic chemistry from Yale University. He has developed resist processes for x-ray mask fabrication, x-ray printing, e-beam direct write, and deep-UV lithography including 248nm and 193nm technologies. He currently manages a group involved in materials and process development for advanced optical applications as well as for the fabrication of optical and x-ray masks. He has been active in a number of conferences including the International Symposium on Electron, Ion, and Photon beams, IEEE Workshop on Microlithography, and is the chair of SPIE's 1997 conference on Emerging Lithographic Technologies.

Dramatic innovation in semiconductor devices and the growth of the microelectronics industry have been driven by steady advancements in microlithography. The shift from i-line to 248nm deep-UV lithography currently occurring in the industry has been made possible by the revolutionary new imaging materials known as chemical amplification (CA) resists invented by H. Ito, one of the prize winners, C. G. Willson and J. M. J. Frechet¹⁾ and by the environmentally stable chemical amplification concept presented by H. Ito, G. Breyta, D. C. Hofer, R. Sooriyakumaran, K. Petrillo and D. Seeger in the award-winning paper.

In the CA system, the decomposition of a dissolution inhibitor (protection group) or cross-linking of a polymer occurs by the acid-catalyzed chain reaction, which provides sought-after high sensitivities and high contrast/resolutions readily²⁻⁷⁾. The development of the CA concept was one of major contributions in the field of resist chemistry and physics, and has had a profound impact on the microelectronics industry as well as micro-lithography.

However, a major obstacle hampered implementation of CA resists in manufacturing. The problem known as the environmental instability arises from the catalytic nature of the imaging mechanisms. This fact has to rouse our interests from the view point of science history. Dr. Ito et al. have assigned many attractive research tasks and has stimulated many resist research scientists into activity as well as realizing the deep-UV lithography. If the CA system had not been developed, the number of research scientists in this field would be much smaller due to the unemployment!

A typical environmental instability, called the postexposure bake delay effect, is the formation of a skin or T-top profile in the positive resist and a linewidth change in the negative resist when the

resist film stands after exposure and before postexposure bake. A trace amount, on the order of 10 ppb, of airborne basic substances absorbed by a resist film interferes with the desired acid-catalyzed reaction.

This award-winning paper presented for the first time a molecular design of an environmentally stable chemical amplification positive (ESCAP) resist⁸⁻¹¹⁾ in a scientific fashion. Identification of the cause of the delay problem (a large free volume in a resist film), a solution to the problem (annealing), difficult annealing of conventional chemical amplification resists due to their thermal and hydrolytic instability, identification and preparation of stable polymer and PAG, and formulation and evaluation of a new ESCAP resist were clearly presented in the paper. In addition to its superb delay stability, the high lithographic performance of the resist was reported in the paper.

The annealing concept and the use of a bulky acid embodied in the ESCAP design have provided valuable guidance to the design of high resolution resists. The ESCAP system has been developed into commercial deep-UV resist products and will be continuously used for the future 193nm deep-UV, electron-beam and x-ray resists¹²⁾.

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