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Diazonaphthoquinone-based Resists

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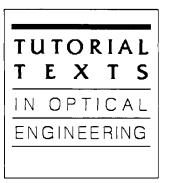

Volume TT 11

SPIE Optical Engineering Press

A Publication of SPIE—The International Society for Optical Engineering
Bellingham, Washington USA

Library of Congress Cataloging-in-Publication Data

Dammel, Ralph, 1954–
Diazonaphthoquinone-based resists / Ralph Dammel.
p. cm. — (Tutorial texts in optical engineering : v. TT 11)
Includes bibliographical references and index.
ISBN 0-8194-1019-5
1. Photoresists. 2. Masks (Electronics) I. Title. II. Series.
TK7874.D34 1993
621.3815'31—dc20 92-25724
CIP

Published by
SPIE—The International Society for Optical Engineering
P.O. Box 10
Bellingham, Washington 98227-0010

Fifth printing

Printed in the United States of America
PDF ISBN: 9781510607989

Introduction to the Series

These Tutorial Texts provide an introduction to specific optical technologies for both professionals and students. Based on selected SPIE short courses, they are intended to be accessible to readers with a basic physics or engineering background. Each text presents the fundamental theory to build a basic understanding as well as the information necessary to give the reader practical working knowledge. The included references form an essential part of each text for the reader requiring a more in-depth study.

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As the series develops, a broad spectrum of technical fields will be represented. One advantage of this series and a major factor in the planning of future titles is our ability to cover new fields as they are developing, giving people the basic knowledge necessary to understand and apply new technologies.

Donald C. O'Shea
Georgia Institute of Technology

February 1993

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Preface

In late 1989, I was approached by Terry Montonye of SPIE, who asked if I would be interested in teaching a course on DNQ resist materials at SPIE's Microlithography conference in San Jose. I did not really know why they picked me, of all people, because at that time, most of my published work had been in chemically amplified resist systems. I may be one of the few people who have learned photolithography backwards, going from chemically amplified resists for x-ray and e-beam lithography to deep UV resists, and from there to the diazonaphthoquinone/novolak systems - maybe they were looking for a unique perspective. Since then, the focus of my work has indeed shifted to these classic resists, and with the opportunity for direct comparison, I am amazed again and again at the performance and process stability that can be obtained with the deceptively simple two-component DNQ/novolak system.

At the time, I gladly accepted SPIE's offer, although I knew I was letting myself in for a lot of work: the amount of material published on DNQ/novolak resists is truly staggering. Still, although the field dates back to the 1940's, there have been quite a few recent developments, both as far as the performance of technical resists is concerned, and with regard to a deeper understanding of the structure/activity relationship of the resist components. The extension of the life of near-UV lithography, and hence of DNQ resists, has been the prevailing theme in microlithography in the last decade, a development to which photoresist chemistry has made a major contribution. It is perhaps characteristic of the more mature phase the field is in that further improvements apparently can no longer be guided by empirical engineering alone, but must rely on a deeper understanding of basic phenomena.

Fortunately for me, a number of authors have already undertaken the arduous task of sifting and reviewing the literature. I would like to point out, in particular, the recent books by A. Reiser and W.M. Moreau, and the somewhat older, but still very relevant *Introduction to Microlithography* by L.F. Thompson, C.G. Willson, and M.J. Bowden, from which a generation of photoresist chemists and engineers has learned the ropes. Among more recent original articles, I would like to mention F. Vollenbroek's review of g-line resists, G. Buhr's work on the sulfene mechanism of 4-sulfonate photolysis, the work of the old Monsanto group to whom we owe the secondary structure model, M. Hanabata's series of articles on the relation between novolak structure and performance, the OCG research group's investigations into the chemical nature of the DNQ/novolak interaction, as well as A. Reiser's studies of the novolak dissolution mechanism and his application of percolation theory to the problem. All of the above I have used, perused, and sometimes abused for inspiration. I am also indebted to my colleagues at Hoechst AG and Hoechst Celanese Corporation for their support, and for setting me straight when I erred. Most of all I am indebted to my family, who every year had to put up with an absentee father in the weeks before the course notes were due.

The course on which the book is based was first presented at the 1990 SPIE Microlithography conference, and was updated and considerably expanded for the 1991 meeting. In December 1990, SPIE initiated the "Tutorial Texts" series of books intended to further enhance the value of their Short Courses by providing participants with course materials that went beyond simple copies of the transparencies used. The series editor, Donald C. O. Shea, and Eric Pepper of SPIE Press suggested that I make the course notes over into a book for the new series. Again, I accepted (sometimes I feel like I have a speech impediment - I cannot say no). The original publication date was planned for the 1992 conference, but books have a way of taking longer to finish than publishers (and authors!) like, and we will just sneak in under the wire for the 1993 Microlithography conference. This would not have been possible but for the efforts of Rick Hermann at SPIE Press, for which I am truly grateful.

Over time, the book has grown beyond what can be taught at reasonable speed in a Short Course, and I am glad that now, having a bound volume to fall back on, I will be able to be teach more selectively. Historically, the audience of the course has been very diverse, from college graduates just entering the field to some of the people whose work I am quoting, and the expectations have ranged from in-depth treatments of chemical mechanisms to a no-nonsense troubleshooting guide for the daily fab routine. I have tried to strike a balance between these extremes, using as a guideline that understanding what goes on in a resist is the best route to fixing, and avoiding, process errors. I therefore believe that not only resist chemists, but everybody will be able to find something of interest in these pages, and I hope that some of the excitement I feel for the intricate and delicate world of DNQ/novolak systems will carry over through these pages to the reader.

Coventry, Rhode Island, February 1993

Ralph Dammel