

Diazonaphthoquinone-based Resists

Books in the SPIE Tutorial Texts Series

Image Formation in Low-Voltage Scanning Electron Microscopy

L. Reimer (1993)

Diazonaphthoquinone-based Resists

Ralph Dammel (1993)

Infrared Window and Dome Materials

Daniel C. Harris (1992)

An Introduction to Morphological Image Processing

Edward R. Dougherty (1992)

An Introduction to Optics in Computers

Henri H. Arsenault and Yunlong Sheng (1992)

Digital Image Compression Techniques

Majid Rabbani and Paul W. Jones (1991)

Aberration Theory Made Simple

Virendra N. Mahajan (1991)

Single Frequency Semiconductor Lasers

Jens Buus (1991)

An Introduction to Biological and Artificial Neural Networks for Pattern Recognition

Steven K. Rogers and Matthew Kabrisky (1991)

Laser Beam Propagation in the Atmosphere

Hugo Weichel (1990)

Infrared Fiber Optics

Paul Klocek and George H. Sigel, Jr. (1989)

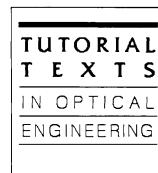
Spectrally Selective Surfaces for Heating and Cooling Applications

C. G. Granqvist (1989)

Diazonaphthoquinone-based Resists

Ralph Dammal
Hoechst Celanese Corporation

Donald C. O'Shea, Series Editor
Georgia Institute of Technology



Volume TT 11



S P I E O P T I C A L E N G I N E E R I N G P R E S S

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

Copyright© 1993 The Society of Photo-Optical Instrumentation Engineers

All rights reserved. No part of this publication may be reproduced or distributed in any form or by any means without written permission of the publisher.

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.

Many of the books in the series will be aimed at readers looking for a concise tutorial introduction to new technical fields, such as CCDs, sensor fusion, computer vision, or neural networks, where there may be only limited introductory material. Still others will present topics in classical optics tailored to the interests of a specific audience such as mechanical or electrical engineers. In this respect the Tutorial Text serves the function of a textbook. With its focus on a specialized or advanced topic, the Tutorial Text may also serve as a monograph, although with a marked emphasis on fundamentals.

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

Table of Contents

Preface to the Series

Table of Contents

Preface

Chapter 1

Introduction	1
1.1 References	8

Chapter 2

Basic Chemistry of DNQ/Novolak Resists	9
2.1 Chemistry of Diazonaphthoquinones (DNQs)	12
2.1.1 Chemical Structure of DNQs	12
2.1.2 Synthesis of DNQs	13
2.2 Photochemistry of DNQs	15
2.2.1 Absorption Characteristics	15
2.2.2 Photochemical Transformation of DNQ-5-sulfonates	19
2.2.3 Photochemical Transformations of DNQ-4-sulfonates	24
2.3 References	27

Chapter 3

Basic Chemistry of Novolaks	29
3.1 Novolak Synthesis	29
3.2 Influence of Novolak Structural Factors on Photoresist Performance	33
3.3 The Secondary Structure Model	41
3.4 Experimental Methods for Measuring Novolak Dissolution Rates	48
3.5 Phenomenological Description of Novolak Dissolution	51
3.6 Novolak Hyperacidity	58
3.7 Dissolution Channels, Critical Deprotonation and Percolation	61
3.8 Quantitative Application of Percolation Theory	62
3.9 References	67

Chapter 4

DNQ/Novolak Interactions	70
4.1 Dissolution Inhibitors as a Perturbation of the Percolation Field	70
4.2 Molecular Basis for DNQ/Novolak Interactions	73
4.3 Why DNQ is Not an Inhibitor	78
4.5 Multi-Step Model for Resist Inhibition/Dissolution	84
4.6 The Polyphotolysis Effect	85
4.7 Structure-Activity Relationships in PAC Backbones	90
4.8 References	96

Chapter 5	
Step-by-step View of the Lithographic Process	97
5.1 Storage and Shelf Life of DNQ/Novolak Resists	97
5.2 Substrate Preparation	99
5.3 Spin Coating	103
5.4 Prebake	104
5.5 Exposure	106
5.6 Post-Exposure Bake	110
5.7 Development	112
5.8 Post-Development Bake	118
5.9 Dry Etching	121
5.10 Stripping	124
5.11 References	124
Chapter 6	
Advanced Processing Schemes for DNQ Resists	126
6.1 Reasons for Using Advanced Processing Schemes	126
6.2 Dyed Resists: To Dye or Not To Dye	126
6.3 Antireflective Layers and Coatings	127
6.4 Top Antireflective Coatings (TARs)	131
6.5 Contrast Enhancement Layers (CEL)	134
6.6 Portable Conformable Mask (PCM) and Built-in Mask (BIM) Schemes	136
6.7 Image Reversal	140
6.8 Profile Modification Methods	145
6.9 Multi-Layer Techniques Involving Dry Etching	145
6.10 Top-Layer Imaging Using Dry Development	149
6.10.1 The DESIRE Process	150
6.10.2 The PRIME Process	153
6.10.3 The Top-CARL Process	154
6.10.4 SUPER Using Patternwise Esterification	156
6.10.5 Relative Importance of Top-Layer Imaging Schemes	157
6.11 Three-Dimensional Images in an Acid-Hardening Resin	157
6.12 Relative Importance of Advanced Processing Schemes	158
6.13 References	160
Chapter 7	
Outlook on DNQ/Novolak Systems	162
7.1 Resolution and Depth-of-Focus	162
7.2 DNQ-Resists in Phase Shift Technology	169
7.3 Annular and Quadrupole Illumination	175
7.4 DNQ-Resists in Deep UV Technology	179
7.5 DNQ-Systems as X-Ray and E-Beam Resists	181
7.6 DNQ-Resists for Laser Direct-Write Applications	184
7.7 Future of DNQ-Based Resists	185
7.8 References	187
Index	189

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