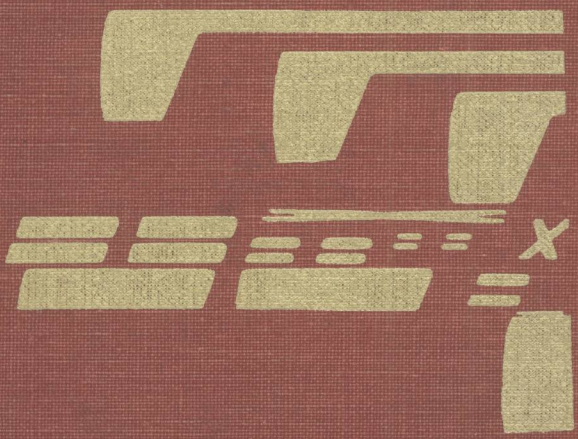
Materials for Microlithography



ACS SYMPOSIUM SERIES 266

Materials for Microlithography

Radiation-Sensitive Polymers

L. F. Thompson, EDITOR
AT&T Bell Laboratories

C. G. Willson, EDITOR
International Business Machines Corporation

J. M. J. Fréchet, EDITOR
University of Ottawa

Based on a symposium cosponsored by the
Division of Polymeric Materials Science and Engineering
and the Division of Polymer Chemistry
at the 187th Meeting
of the American Chemical Society,
St. Louis, Missouri,
April 8–13, 1984

American Chemical Society, Washington, D.C. 1984

Library of Congress Cataloging in Publication Data

Materials for microlithography.
(ACS symposium series, ISSN 0097-6156; 266)

Includes bibliographies and indexes.

1. Polymers and polymerization—Congresses. 2. Photoresists—Congresses. 3. Lithography—Congresses. 4. Microelectronics—Materials—Congresses.

I. Thompson, L. F., 1944– . II. Willson, C. G. (C. Grant), 1939– . III. Fréchet, J. M. J. IV. American Chemical Society. Division of Polymeric Materials: Science and Engineering. V. American Chemical Society. Division of Polymer Chemistry. VI. American Chemical Society. Meeting (187th: 1984: St. Louis, Mo.) VII. Series. VIII. Title: Radiation-sensitive polymers.

TK7871.15.P6M37 1984 621.381'73 84-21744
ISBN 0-8412-0871-9

ACS Symposium Series

M. Joan Comstock, *Series Editor*

Advisory Board

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable since symposia may embrace both types of presentation.

PREFACE

THE CONTINUING MINIATURIZATION OF ELECTRONIC DEVICES shows little sign of abating. Currently, devices containing over 1,000,000 transistors are manufactured with minimum circuit features of 1.0–1.25 μm. The circuit elements are fabricated by a series of processes known collectively as lithography. During the past several years the term microlithography has been used increasingly to denote the trend toward decreasing feature sizes. The technology used today continues to be dominated by traditional photolithographic techniques, but most scientists and engineers in the semiconductor industry are convinced that devices with dimensions less than 1 μm will be required in the near future, and that new technologies will be required to fabricate them. These new technologies will likely be a combination of entirely new exposure techniques such as electron-beam, X-ray, or deep-UV lithography coupled with significant modifications of conventional UV processes. These modifications will most likely use multilayer schemes.

Polymeric materials, especially the radiation-sensitive polymers, lie at the heart of all of these new technologies. For the first time, it will be necessary for the development engineer as well as the scientist to possess a thorough understanding of the chemistry of radiation-sensitive polymers. This book provides the foundation for such an understanding. Although the book is based on research papers presented at a symposium, it has been constructed with considerable introductory material and considerable editing with the result that it is more of a unified text than a compilation of research papers.

Three extensive introductory chapters by Everhart, Broers, and Bowden provide a solid foundation in the physics and chemistry of the lithographic process together with an overview of current resist systems. These 3 chapters, coupled with 20 chapters from outstanding radiation polymer chemists throughout the world, provide a firm basis for understanding the important fundamental concepts in radiation chemistry as applied to design, development, and application of resist materials.

The authors and editors are indebted to the AT&T Bell Laboratories Text Processing Group, especially Susan Pope and Carmela Patuto. Special thanks are due to AT&T Bell Laboratories Art Department and Roy T.

Anderson who coordinated all of the art work. Special acknowledgment also goes to Bonnie Cahill who handled most of the administrative aspects in preparing this volume.

L. F. THOMPSON
AT&T Bell Laboratories
Murray Hill, NJ 07974

C. G. WILLSON
IBM Research
San Jose, CA 95193

J. M. J. FRECHET
University of Ottawa
Ottawa, Ontario
K1N-9B4, Canada

August 1984

CONTENTS

INTRODUCTION

Introduction

Within the next few years, production quantities of devices will be commercially available which contain structures less than 1.0 microns. To accomplish this, new microlithography technologies will be required and these new technologies will require new resist (radiation sensitive polymers) systems and/or processes. The purpose of this book is to provide the scientist and engineer with the fundamental knowledge base that underlies resist design and present some of the newer approaches being investigated. This may be better appreciated through an understanding of the physics and chemistry of the lithographic process along with a historical perspective on materials for fine line lithography which forms the subject of the first three chapters of this book.

In Chapter 1, Tom Everhart (Cornell) reviews his work on the fundamental limits of lithography based on a statistical theory. This theory provides the basic limitation of sensitivity and defects.

In Chapter 2, Alec Broers (IBM) discusses fundamental limitations that are imposed by engineering considerations of hardware design. These limitations affect the economical feasibility of a particular lithographic strategy, an understanding of which is necessary in order to choose between the many complex and competing alternatives.

In Chapter 3, Murrae Bowden (Bellcore) presents a comprehensive perspective on resist materials currently used in microlithography research and development.

The reader is strongly urged to read these three chapters first as they provide the context within which the following chapters which deal with specific new research in radiation chemistry and application to resist design may be better understood.

1

Fundamental Limits of Lithography

T. E. EVERHART

College of Engineering
Cornell University, Ithaca, NY 14853

Fine lithographic patterns are produced when radiation (photons, electrons, ions, or neutral particles) interacts with a material, and produces physical or chemical changes (or both) in that material selectively, as required to replicate the desired pattern. The type and energy of radiation is important to characterize the process, the amount of radiation (exposure) generally must be controlled, and the resulting removal of material by physical or chemical means must also be controlled. Photons generally interact with materials somewhat differently than electrons, which are again different than ions, as momentum of the incoming radiation increases from photon to electron to ion. The incoming radiation excites electrons in the material, and these generally produce the chemical changes "developed" by dry or wet chemical processes in many forms of lithography. The volume of material exposed by the incoming radiation depends on how it penetrates the material being exposed, how it is scattered by the material it is penetrating, and how far secondary electrons that are excited by the incident radiation travel in the material while they are energetic enough to produce exposure.

Patterns can be produced in a mask, and that mask used to define the pattern to be produced on the material to be exposed. Alternatively, particle beams can be deflected in patterns over the substrate to be exposed, and the patterns are produced by turning the beam off and on, changing its shape and size, or both. Regardless of how the pattern is produced, and regardless of the type of radiation used, there are some fundamental aspects of exposure that hold for all lithographic systems, and these are the topic of this chapter.

If photons are the exposing radiation, the energy loss of the photons as they penetrate the material will determine the excitation of secondary electrons, and subsequent exposure of the resist material. The energy loss per unit length will depend upon the energy of the photons, and must be known. Often the useful exposure produced by incoming photons is determined experimentally, and it is assumed here that such dose information to produce correct exposure is known. If electrons are the exposing radiation, the energy loss is again related to the incoming energy of the electrons, and the transverse scatter also affects not only the transverse resolution of the fine lines of the pattern, but also energy dosage per unit depth delivered to the material to be exposed. Similar statements can be made for incoming ions. Ions generally do not scatter

Current address: University of Illinois, Urbana, IL 61801

0097-6156/84/0266-0005$06.00/0

transversely in nearly the same degree that lighter electrons do, and they lose energy in much shorter distances, hence for a given incident energy, ions penetrate much less into the material, but deliver much more dose per incident particle.

We shall develop a fundamental relationship between the dose Q delivered to the resist, the number of particles N striking the pixel (picture element or elementary area to be exposed in the resist), the flux of radiation delivering the exposure dose, the time required to expose a pixel, and the dimension of the pixel. To be specific, we shall consider the case of electrons exposing a resist, and shall strive to provide intuitive insight, rather than an absolutely precise mathematical formulation.

In order to be certain we have produced a significant difference between an exposed pixel and a pixel that is not exposed, a certain number of incident photons, electrons, or ions must each produce an effect in the volume of resist underlying that pixel. This means that if the resist requires a dose of Q coulombs/cm^2 for correct exposure, it also requires a minimum number of electrons N_m to strike and lose their energy in each pixel so that each pixel receives the minimum necessary exposure on statistical grounds. Therefore, if l_p is the pixel linear dimension and e is the electronic charge,

$$Q/e \geqslant \left(N_m/l_p{}^2\right) \tag{1}$$

Equation 1 states a very important point, namely, the exposure dose must always exceed a minimum value, and the smaller the pixel dimension, the larger that minimum value must be. This is a well-known phenomena in photography, for example, since very high resolution film is much less sensitive than lower resolution, or "fast" film. Put another way, Equation 1 explains why large grain size goes with "fast" film, and high definition goes with "slow" film. Since the dose must increase as the pixel dimension decreases for the probability that each pixel will be correctly exposed to remain constant, high resolution resists are expected to be "slower" (i.e., require larger doses) than lower resolution resists. Put yet another way, based only on pixel signal-to-noise ratio considerations only, the minimum total number of electrons needed to reliably expose a pattern of a given complexity is independent of the size of the pixel. More sensitive resists are useful for larger pixels, and less sensitive must be used for smaller pixels. This argument assumes that an electron's energy is lost within a pixel, i.e., that the transverse scattering is considerably smaller than a pixel, and that the beam size is at least as small as a pixel.

Next, consider the time required to expose a pattern with a focused electron beam. The electron beam with current density J (A/cm^2) must strike a pixel for time τ(sec) to produce exposure Q (coulombs/cm^2) = $J\,\tau$. The beam current density is

$$J = J_c(\text{eV/kT})\ \alpha^2 \tag{2}$$

after Langmuir, where J_c, T, and V are cathode current density, temperature, and beam accelerating voltage, e and k are the electronic charge (1.6×10^{-19} coulombs) and Boltzmann's constant (1.38×10^{-23} J/°K), and α is the beam convergence angle.

By increasing α, the current density exposing the pattern increases, which is desirable. However, if α is increased too far, the beam spot diameter increases because of the spherical aberration of the focusing system. An optimum value of α occurs when the diameter of the disk of confusion due to spherical aberration, $d_s = 0.5\, C_s\alpha^3$ (C_s is the spherical aberration coefficient), is set equal to the gaussian spot diameter, $d_s = d_g = \ell_p/\sqrt{2}$. Using the normal approximation of adding spot diameters in quadrature, the total spot size then is $d = \left[d_s^2 + d_g^2\right]^{1/2} = \ell_p$, the pixel dimension. The optimum convergence angle is then

$$\alpha_{opt} \simeq \left[\frac{\sqrt{2}\,\ell_p}{C_s}\right]^{1/3}, \tag{3}$$

and the exposure in time τ is

$$Q = J\tau = J_c\,\frac{\mathrm{eV}}{\mathrm{kT}}\left[\frac{\sqrt{2}\,\ell_p}{C_s}\right]^{2/3}\tau = \frac{\beta\pi 2^{1/3}}{C_s{}^{2/3}}\,\ell_p{}^{2/3}\tau\,, \tag{4}$$

where β is the electron optical brightness ($J_c\mathrm{eV}/\pi\mathrm{kT}$). Equation 4 gives the change density deposited in a spot of diameter ℓ_p in time τ. For resist exposure, this charge density must equal the resist sensitivity under the exposure conditions used.

To ensure that each pixel is correctly exposed, a minimum number of electrons must strike each pixel. Since electron emission is a random process, the actual number of electrons striking each pixel, n, will vary in a random manner about a mean value, $\bar{n}$. Adapting the signal-to-noise analysis found in Schwartz (1959) to the case of binary exposure of a resist, one can show straightforwardly that the probability of error for large values of the mean number of electrons/pixel $\bar{n}$ is $e^{-\bar{n}/8}/[(\pi/2)\bar{n}]^{1/2}$. This leads to the following table of probability of error of exposure:

$\bar{n}$	50	100	150	200
Probability of error	2.2×10^{-4}	3×10^{-7}	4.7×10^{-10}	7.8×10^{-13}

To be conservative, we choose $\bar{n} = 200$, which should mean that, on average, no pixels in a field of 10^{10} pixels are incorrectly exposed due to randomness, as long as each electron striking a pixel causes at least one exposure event in the resist. For a pixel of dimension ℓ_p, the minimum number of electrons striking it (= 200 here) to provide adequate probability of exposure is N_m, and the charge density is then $Q = N_m e/\ell_p{}^2$. Substituting into Equation 4 gives

$$N_m e = \frac{\beta\pi 2^{1/3}}{C_s{}^{2/3}}\,\tau\ell_p{}^{8/3} \tag{5}$$

To determine how noise limits pixel dimension, arrange Equation 5 so that normalized exposure time depends on pixel dimension; note that $2^{1/3}\pi \simeq 4$:

$$\left[\frac{4\beta}{N_m e C_s^{2/3}}\right]\tau = \ell_p^{-8/3}. \tag{5a}$$

A corresponding equation for real resist exposure is

$$\left[\frac{4\beta}{N_m e C_s^{2/3}}\right]\tau_R = \frac{Q}{N_m e}\,\ell_p^{-2/3}. \tag{4a}$$

Here the same normalization was chosen for τ to facilitate plotting Equation 4a and 5a on the same figure of τ vs. ℓ_p.

The above paragraphs give the fundamental considerations of electron beam formation and focusing that cause the time, τ, required to expose a pixel to N_m electrons to increase as the pixel linear dimension ℓ_p decreases. As shown by the left-hand curve in Figure 1, $\tau \propto \ell_p^{-8/3}$. To correctly expose a real resist of sensitivity Q coulombs/cm^2, a fixed number of electrons per unit area must strike the resist, and the time required to expose such a resist is $\tau_R \propto \ell_p^{-2/3}$. A family of curves corresponding to such real resist exposure is also shown in Figure 1. For a given probability that each pixel will be correctly exposed, these curves for a real resist cannot extend to the left past the limiting curve. As we proceed to the right of the limiting curve along a curve for constant sensitivity, Q, the number of electrons striking each picture element increases, improving the pixel signal-to-noise ratio. Because the normalization factor on the ordinate of Figure 1 includes N_m, the vertical positioning of the τ_R curves depends on the value of N_m actually chosen. For binary exposure, the probability that a pixel struck by 200 electrons is not correctly exposed is less than 10^{-12}; if struck by 100 electrons, a pixel has a probability of incorrect exposure of 3×10^{-7}, enough to cause many errors in a pattern of 10^{10} pixels. Hence we have set $N_m = 200$ in the τ_R curves of Figure 1.

These curves predict that for $Q = 10^{-8}$ coulombs/cm^2, pixels smaller than $\ell_p = 1.0$ μm should be possible, and for $Q = 10^{-6}$ coulombs/cm^2, pixels below $\ell_p = 0.1$ μm should be attainable, based on a signal-to-noise ratio considerations alone. Resists such as polymethyl methacrylate processed for high resolution by the correct choice of developer have demonstrated linewidths less than 0.1 μm. The fundamental point emphasized here is that slow resists are necessary to get higher resolution, a result familiar to all photographers. Note that if all electron energy is not dissipated within the pixel (due to lateral scattering, for example), the exposure time per pixel increases and the solid curve in Figure 1 moves toward the dashed curve. Inclusion of quantitative information on scattering and aberrations in addition to spherical aberration will cause the actual limiting curve to move toward the right at small pixel dimensions, as shown in Figure 1.

Equations 4a and 5a both show that exposure time can be shortened by increasing the beam brightness, or decreasing the spherical aberration C_s. By plotting these equations in normalized form in Figure 1, absolute pixel