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MOLECULAR THEORY OF LITHOGRAPHY

Uzodinma Okoroanyanwu

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SPIE.

MOLECULAR THEORY OF LITHOGRAPHY

for
Anett and Sophie

Preface

The science and technology of lithography, especially advanced semiconductor lithography, have now reached such an advanced stage of development and promise such numerous applications (as evidenced by the numerous technologies that the field is now enabling—from electronics to photonics, catalysis to medicine, energy transduction and storage to sensing) that there is a need for a single, reasonably complete, unified exposition of the molecular theory that underlies lithographic imaging. This book is intended to fill this need. It attempts to systematically explain with physical-chemical theories the molecular-level interactions that underlie the essential aspects of lithographic imaging phenomena. The effects of such molecular-level interactions become all the more heightened in the regime of single-digit to a few tens of nanometer-patterned feature length scales, a regime that overlaps the radius of gyration of the resist polymers used in the patterning. In addition, the book will provide the theoretical basis for the main unit operations of the advanced lithographic process, as well as for advanced lithographic imaging mechanisms, including photochemical and radiochemical, imprint, and directed self-assembly imaging mechanisms.

The book is intended for students and professionals whose knowledge of lithography extends to the chemistry and physics underlying its various unit operations, and the imaging mechanisms of its various forms. The methods of physical chemistry are used as far as possible; therefore, a certain familiarity with chemical kinetics, thermodynamics, statistical mechanics, and quantum mechanics will be helpful, as will be familiarity with elementary concepts in physics such as energy, force, electrostatics, electrodynamics, and optics. For the rest, the book has also been written to be of service to readers who are not studying the above-named subjects; to this end an effort has been made to be particularly complete with bibliographic references in the text.

I am particularly grateful to Dr. Chris Mack, Editor of the *Journal of Micro/Nanolithography, MEMS and MOEMS*, who read and commented on the entire manuscript and provided numerous suggestions for improvement. I am also grateful to Dr. Manuel Thesen of micro resist technology GmbH, who read parts of the manuscript and provided suggestions for improvement.

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Uzodinma Okoroanyanwu
November 2015

Acronyms and Abbreviations

ACRAM	N-(9-acridinyl) acetamide
AFM	atomic force microscopy
AGTP	aldol group transfer polymerization
AIBN	2,2'-azobis(isobutyronitrile)
ARC	antireflection coating
ATRP	atom transfer polymerization
BARC	bottom antireflection coating
BCP	block copolymer
BOP	benzyloxy-protected poly(<i>p</i> -hydroxystyrene)
BPO	benzoyl peroxide
CAR	chemically amplified resist
CBN	carbo- <i>t</i> -butoxy norbornene
CD	critical dimension
CMTF	critical modulation transfer function
COMA	cycloolefin maleic anhydride
COP	crystal-originated pit
CPS	close-packed sphere
CVD	chemical vapor deposition
DEA	dissociative electron attachment
DEAP	2,2-diethoxyacetophenone
DLVO	Derjguin–Landau and Verwey–Overbeck
DMPA	2,2'-dimethoxy-2-phenylacetophenone
DNQ	diazonaphthoquinone
DOF	depth of focus
DPE	1,1-diphenylethylene
DPPH	1,1-diphenyl-2-picrylhydrazyl
DPSF	diffusion point spread function
DR	dissolution rate
DSA	directed self-assembly
DTBP	di- <i>tert</i> -butyl peroxide
DUV	deep ultraviolet
EBL	electron beam lithography
ESCAP	environmentally stable chemical amplification photoresist

EUV	extreme ultraviolet
EUVL	extreme ultraviolet lithography
FRP	free radical polymerization
FTIR	Fourier transform infrared
GTP	group transfer polymerization
HF	hydrogen fluoride
HM	hard mask
HMDS	hexamethyldisilazane
IC	integrated circuit
IC	internal crossing
ISC	intersystem crossing
ITRS	International Technology Roadmap for Semiconductors
J-FIL™	Jet and Flash Imprint lithography
KRS	ketal resist system
KTFR	Kodak Thin Film Resist
LEE	low-energy electrons
LEEPL	low-energy electron projection lithography
LPP	laser-produced plasma
LTEM	low thermal expansion material
LV	liquid–vapor (interface)
MA	methacrylic acid
MEMS	micro-electromechanical system
MIF	metal ion free
MMA	methyl methacrylate
MOP	methoxypropyl-protected poly(<i>p</i> -hydroxystyrene)
MTF	modulation transfer function
NA	numerical aperture
NBHFA	norbornene hexafluoroisopropanol
NHA	numerical half aperture
NILS	normalized image log-slope
NLLO	neutral layer lift-off
ODT	order–disorder transition
OPC	optical proximity correction
OPD	optical path difference
PAC	photoactive compound
PAG	photoacid generator
PBOCST	poly(4- <i>tert</i> -butoxycarbonyloxystyrene)
PBS	poly(1-butene sulfone)
PD	polydispersity
PDDA	<i>p</i> -phenylenediacrylic acid
PDI	polydispersity index
PDMS	poly(dimethylsiloxane)
PEB	post-exposure bake
PEP	poly(ethylene propylene)

PET	poly(ethylene terephthalate)
PGMA	poly(glycidyl methacrylate)
PGMEA	propylene glycol monomethyl ether acetate
PHOST	poly(4-hydroxystyrene)
PHS	poly(4-hydroxyl styrene)
PHStBOC	poly(4- <i>tert</i> -butoxycarbonyloxystyrene)
PI	polyisoprene
PIL	photoimprint lithography
PL	perforated layer
PMIPK	poly(methyl isopropenyl ketone)
PMMA	poly(methyl methacrylate)
PMPS	poly(methylpentene sulfone)
POSS	polyhedral oligomeric silsesquioxane
PPDA	phenylenediacrylic acid
PPO	1-phenyl-1,2-propanedione-2- <i>O</i> -benzoyloxime
PR	photoresist
PS	poly(styrene)
PTFE	poly(tetrafluoroethylene)
PVP	poly(vinyl pyridine)
R2R	roll-to-roll
RDPSF	reaction–diffusion point spread function
RIE	reactive ion etching
ROMP	ring-opening metathesis polymerization
RTNB	resist trim and neutral brush
SAM	self-assembled monolayer
SANS	small-angle scattering
SC	supercritical
SCMFT	self-consistent mean-field theory
S-FIL [®]	Step and Flash Imprint Lithography
SFRP	stable free-radical polymerization
SL	solid–liquid (interface)
SNS	sulfone/novolac system
STM	scanning tunneling microscope
SV	solid–vapor (interface)
TBEST	<i>tert</i> -butyl ester-protected 4-hydroxystyrene
TBMA	<i>tert</i> -butyl methacrylate
TBOC	<i>tert</i> -butoxycarbonyl
TE	transverse electric
TEMPO	tetramethylpiperidinoxy
TFE	tetrafluoroethylene
THF	tetrahydrofuran
THP	tetrahydropyranal
TIL	thermal imprint lithography
TM	transverse magnetic

TMAH	tetramethylammonium hydroxide
TMS	trimethylsilyl
TMSDEA	trimethylsilyldiethylamine
TPSHFA	triphenylsulfonium hexafluoroantimonate
UTR	ultrathin resist
UV	ultraviolet
UV-IL	ultraviolet imprint lithography
VAP	vinyl addition polymerization
VBC	vinylbenzyl chloride
VUV	vacuum ultraviolet
WLF	Williams–Landel–Ferry
X-PS	cross-linkable polystyrene
ZEP	poly(chloro-acrylate- <i>co</i> - α -methylstyrene)

Table of Contents

<i>Preface</i>	<i>xvii</i>
<i>Acronyms and Abbreviations</i>	<i>xix</i>
1 Overview of Lithography	1
1.1 Introduction	1
1.2 The Lithographic Process	2
1.3 Advanced Lithographic Patterning Techniques and Imaging Mechanisms	5
1.3.1 Optical lithography	5
1.3.1.1 Elements of optical lithography	6
1.3.1.1.1 g-line (436 nm), h-line (405 nm), and i-line (365 nm) lithographies	7
1.3.1.1.2 KrF (248 nm) lithography	7
1.3.1.1.3 Dry ArF (193 nm) lithography	7
1.3.1.1.4 Water-immersion ArF (193-nm) lithography	8
1.3.2 Extreme ultraviolet lithography	10
1.3.3 Electron beam lithography	12
1.3.3.1 Electron beam lithography system	13
1.3.4 Ion beam lithography	15
1.3.5 Imprint lithography	17
1.3.5.1 Thermal imprint lithography	18
1.3.5.2 Photoimprint lithography	19
1.3.5.2.1 Soft lithography	20
1.3.5.2.2 Hard PIL—Jet and Flash Imprint Lithography	21
1.3.5.3 Roll-to-roll photoimprint lithography (R2R-PIL)	22
1.3.6 Molecular self-assembly lithography	24
1.3.6.1 Block copolymer self-assembly lithography	25
2 Theory of the Lithographic Process	31
2.1 Introduction	31
2.2 Adhesion Promotion	31
2.3 Resist Coating	36
2.3.1 Resist spin-coating process	36

2.3.2	Characteristics of thin resist films	40
2.3.3	Instabilities in UTR films	42
2.3.3.1	Spin coating and instabilities in UTR films	42
2.3.3.2	Hydrodynamics of UTR films	43
2.3.3.3	Instabilities and thermophysical properties of UTR films	45
2.4	Soft Bake	47
2.5	Alignment	49
2.6	Exposure	50
2.6.1	Basic imaging theory	50
2.6.2	Aerial image formation	54
2.6.2.1	Aerial image formation models	55
2.6.2.1.1	Scalar and vector models for calculating aerial image intensity	55
2.6.3	Standing wave models	55
2.6.4	Image formation in the resist	60
2.6.5	Continuum modeling of latent image formation in the resist	64
2.6.5.1	Exposure models	66
2.6.5.2	Exposure chemistry of DNQ resists	70
2.6.5.2.1	Post-exposure bake of DNQ resists	75
2.6.5.2.2	Post-exposure bake diffusion models	76
2.6.5.3	Exposure reaction and chemical amplification reaction	79
2.6.5.3.1	Photoacid diffusion	82
2.6.5.3.2	Accounting for the effects of acid loss	85
2.6.5.3.3	Accounting for the effects of quenchers	87
2.6.5.3.4	Solving acid–base reaction–diffusion equations	87
2.6.5.3.5	Experimental elucidation of deprotection kinetics of a representative resist polymer system	89
2.6.5.3.6	Monitoring photoacid generation in thin photoresist films by means of fluorescence spectroscopy	94
2.6.6	Stochastic modeling of latent image formation in resists	96
2.6.6.1	Photon shot noise	97
2.6.6.2	Stochastic treatment of photon absorption and exposure	98
2.6.6.3	Stochastic treatment of acid diffusion in conventional resists	99
2.6.6.4	Stochastic treatment of acid-catalyzed reaction–diffusion in chemical amplification resists	100
2.7	Development	100
2.7.1	Resist development methods	102
2.7.2	The nature of the development process	103
2.7.3	Solubility switching approaches to realizing contrast between exposed and unexposed regions of the resist during development	105

2.7.4	Types of development in resist processing	107
2.7.4.1	Chemical development in resist processing	107
2.7.4.2	Physical development in resist processing	108
2.7.5	Kinetics and mechanism of resist polymer dissolution	108
2.7.5.1	Dissolution mechanism of phenolic resists	109
2.7.5.2	Development rate models	111
2.7.5.2.1	Kinetic development model or Mack model	112
2.7.5.2.2	Enhanced kinetic development model or enhanced Mack model	114
2.8	Postdevelopment Bake and Resist Stabilization Treatments	115
2.8.1	Postdevelopment bake	115
2.8.2	UV radiation curing	117
2.8.3	Electron beam curing of resists	119
2.8.3.1	Radiation chemistry of electron beam curing	120
2.8.3.2	Effects of electron beam curing	122
3	Theory of Molecular Interactions in Lithography	123
3.1	Introduction	123
3.2	Combining Relations and Interactions that Determine the Solubility Switch and Contrast in Lithographic Resist Systems	125
3.3	Molecular Solubility Modulation and Lithographic Contrast	129
3.3.1	Molecular solubility modulation	129
3.3.2	Lithographic contrast	130
3.4	Molecular Interactions in Lithography	131
3.4.1	General van der Waals interactions operating during resist film PEB and development in the developer solution medium	133
3.4.1.1	Van der Waals interaction between a polymer molecule and a flat solid resist film surface composed of the same polymeric molecule	136
3.4.1.2	Van der Waals interactions operating between molecules during resist PEB and development in the developer solvent medium	138
3.4.1.3	Interactions operating between a charged ionic species and solid resist film surface during resist development in the developer solvent medium	145
3.4.2	General electrostatic interaction forces operating in resist solvent development	147
3.4.2.1	Case 1: Charged resist surface in water with no added electrolyte	149
3.4.2.2	Case 2: Charged resist surface in TMAH electrolyte solutions	153
3.4.2.3	Coulombic interactions between ions within the developer solution	157

3.4.2.4	Electrostatic double-layer interactions between ions or charged small molecules in developer solution	157
3.4.2.5	Electrostatic interaction between resist film surface with polar functional groups and spherical particles or macromolecules in the developer	159
3.4.3	Van der Waals and double-layer electrostatic interactions between the resist and developer, and between charged species in the developer	161
3.4.4	Hydrophobic interaction forces operating during resist solvent development	162
3.4.5	Steric interactions	164
3.4.6	Hydration interactions	164
3.4.7	Acid–base interactions	165
3.4.8	Hydrogen bonding interactions	165
3.5	Overall Developer–Resist Interaction Potential and the Dissolution Process	166
3.5.1	Estimating the overall interaction energy of the developer–resist film system	168
3.6	Resist Dissolution Process	171
3.6.1	Thermodynamics of resist polymer dissolution	176
3.6.1.1	Entropy of mixing resist polymeric solutes dissolved in developer solvent	178
3.6.1.2	Enthalpy of mixing developer solvent and resist polymeric solute	181
3.6.1.3	Free energy of mixing resist polymeric solute with developer solvent	184
3.7	Molecular Interactions Operating in Thermally Driven Diffusion of Photoacids During PEB of Resist Films	186
3.7.1	Interactions between immiscible polymer–polymer interfaces of the exposed and unexposed parts of the resist polymer film	186
3.7.2	Ambipolar diffusion of photoacid ions	187
3.7.3	Acid evaporation at the resist–air interface	190
3.8	Dissolution Properties of Resist Polymers	192
4	Theory of Photochemical and Radiochemical Lithographic Imaging Mechanisms	199
4.1	Introduction	199
4.2	Preliminary Remarks on Resist Photochemistry and Photophysics	200
4.2.1	Quenching processes of excited states	206
4.2.2	Excited-state complexes	208
4.2.2.1	Excimers	208
4.2.2.2	Exciplexes	209
4.2.3	Energy transfer	210
4.2.3.1	Dipole resonance transfer	211
4.2.3.2	Exchange transfer	213