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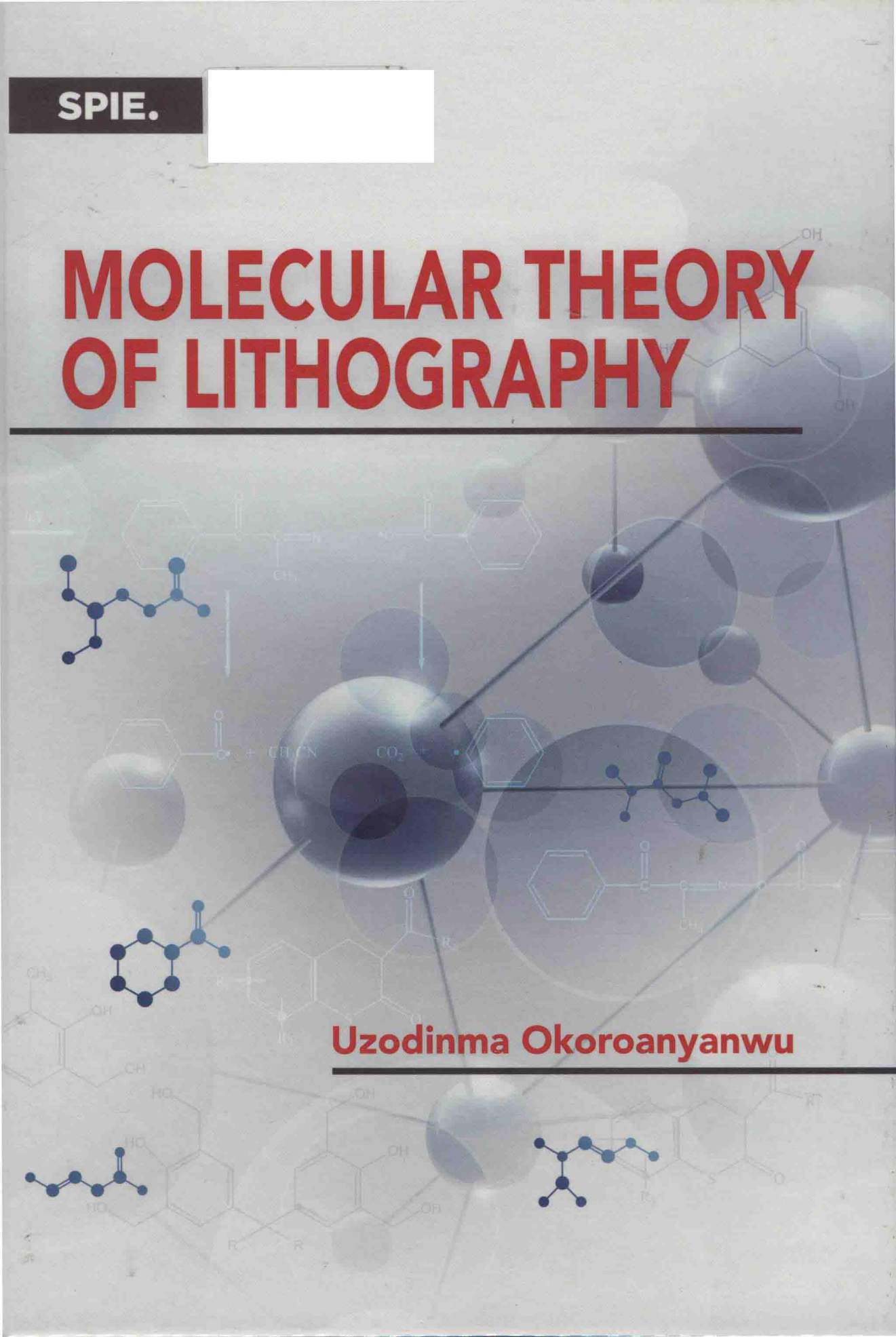
MOLECULAR THEORY OF LITHOGRAPHY



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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.

I would also express my sincere appreciation to the editorial staff of SPIE Press, especially Dara Burrows and Tim Lamkins, who oversaw the production and publication of the book.

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(*p*-hydroxystyrene)
BPO	benzoyl peroxide
CAR	chemically amplified resist
CBN	carbo-*t*-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-*tert*-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(*p*-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-*tert*-butoxycarbonyloxystyrene)
PBS	poly(1-butene sulfone)
PD	polydispersity
PDDA	*p*-phenylenediacrylic acid
PDI	polydispersity index
PDMS	poly(dimethylsiloxane)
PEB	post-exposure bake
PEP	poly(ethylene propylene)

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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-*tert*-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 silsequioxane
PPDA	phenylenediacrylic acid
PPO	1-phenyl-1,2-propanedione-2-*O*-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	*tert*-butyl ester-protected 4-hydroxystyrene
TBMA	*tert*-butyl methacrylate
TBOC	*tert*-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	trimehylsilyldiethylamine
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 polysterene
ZEP	poly(chloro-acrylate-*co*-α-methylstyrene)

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