Chemistry and Lithography
Chemistry and Lithography

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Dedicated to the memory of the late Professor William C. Gardiner, Jr.,
of The University of Texas at Austin, under whom I studied.
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Preface

It is my intention to provide in this book a concise treatment of chemical phenomena in lithography in a manner that is accessible to a wide readership. While the emphasis is placed on how lithography is mediated through chemical phenomena, topics in optical and charged particle physics as they are practiced in lithography are also presented, with a broader view to illustrate how the marriage between chemistry and optics has made possible the print and electronic revolutions on which our digital age depends.

The link between chemistry and lithography is essentially fourfold. First, several important chemical and physical principles were involved in the invention of lithography and photolithography. This theme is explored in Part I, covering Chapters 1–4. Chapter 1 introduces the role of lithography in print and electronic revolutions. Chapter 2 deals with the invention of lithography and photolithography. Chapter 3 provides the background surrounding the discovery of the chemical and optical principles that made possible the invention of lithography and photolithography. Chapter 4 traces the evolution of lithography from its invention to the various forms in which it is practiced today.

Second, the processes for the synthesis, manufacture, usage, and handling of lithographic chemicals and materials are all chemical transformations, involving distinct chemical reactions that follow well-established chemical principles. This theme is explored in Part II, covering Chapters 5–9. Chapter 5 deals with synthesis and formulation of the chemicals used in lithography such as inks, fountain solutions, resists, antireflection coatings, solvents, developers, resist strippers and removers, etc. Chapters 6 and 7 explore the chemistry of negative and positive resist materials, respectively, in terms of their synthesis, physical characterization, radiation chemistry, imaging mechanism, and lithographic applications. Chapter 8 explores in a general manner the radiation and photochemistry of resist materials. Chapter 9 deals with the theory and application of antireflection coatings in reflectivity control.

Third, several important chemical and physical principles are involved in the various modules that constitute lithography, covering preparation of the lithographic substrates (be they lithographic plates or silicon wafers), coating and deposition of resist solutions on appropriate substrates affording thin dry films, exposure of the dry films to actinic radiation, thermal processing of the exposed films, development of the exposed and baked films to afford the
lithographic relief images, and postdevelopment processes designed to stabilize the relief images against subsequent processes. These themes are explored in detail in Part III, dealing with the practice of lithography as exemplified in stone plate and offset lithography on one hand, and semiconductor lithography on the other. These topics are covered in Chapters 10–17.

Chapter 10 deals with stone and offset lithographic processing that is employed in the printing of fine art images, newspapers, textbooks, advertisements, etc. By far, the most advanced form of lithography practiced today is semiconductor lithography, used in the fabrication of logic and memory integrated circuit (IC) devices that power computers, cell phones, telecommunications systems, and a host array of other devices. For this reason, Chapter 11 is entirely dedicated to a discussion on the overview of the semiconductor lithographic process, covering all of the chemical and physical phenomena involved in all of the related unit operations. In particular, the physical characterization of these processes as well as the photochemistry and photophysics involved in the exposure processes are highlighted. Chapter 12 deals with lithographic modeling. Chapter 13 in turn deals with optical lithography, which by far is the most dominant of all of the semiconductor lithographic techniques. Covering g-line, i-line, KrF, ArF, and F₂ lithographies, the discussion here focuses on the physics and chemistry of the exposure sources, the construction of the exposure tool, mask making, and application of these lithographies in device manufacture. Chapter 14 deals with x-ray and EUV lithographies. Chapter 15 presents charged particle lithographies based on electron beams and ion beams.

Chapter 17 explores the chemistry underlying advanced resist processing techniques, including resist-based resolution enhancement techniques (such as double patterning, chemical amplification of resist line or the CARL process, hydrophilic overlayer or the HOL process, reflow techniques, etc.) and stabilization techniques (such as UV, e-beam curing, and ion implantation) used to improve the quality of semiconductor lithographic patterning. In such techniques, the chemistry is often quite different from that used in conventional resist processing. This is one of the most active areas of current research, and one in which it appears likely that employing postexposure resist chemical modifications might prove successful in overcoming resolution limits imposed by the constraints of the geometric optics of the exposure tool.

Chapter 17 also discusses the chemical and physical basis of emerging patterning challenges confronting lithography as the industry transitions to lithographic nodes where the physical properties of the resist become extremely sensitive to the substrate and interfacial and confinement effects. These effects begin to manifest as the thickness of the resist film approaches a few multiples of the radius of gyration of the polymers from which they are constituted. Such challenges include resolution loss due to uncontrolled diffusion, thin-film instabilities and confinement effects, line edge roughness, etc. Other equally important challenges, but not altogether related to resist film thickness, include the impact of oxygen on lithographic patterning, contamination (airborne, water, resist outgas, particle, inorganic salts, etc.), pattern collapse, line width slimming, etc. These are covered in Chapter 13.
The fourth link between chemistry and lithography concerns the principles governing the chemical transformations utilized in process-integration schemes that are part of the implementation of lithography in IC device fabrication. This theme, discussed in Chapter 16, explores how lithography is used to define and pattern the various front end of lithography (FEOL) and back end of lithography (BEOL) layers of a state-of-the-art Advanced Micro Devices (AMD) microprocessor based on a complementary metal-oxide semiconductor (CMOS) device.

An attempt has been made throughout the book to provide examples illustrating the diversity of chemical phenomena in lithography across the breadth of the scientific spectrum, from fundamental research to technological applications. The format of this book is not necessarily chronological, but is such that related aspects of lithography are thematically organized and presented with a view to conveying a unified view of the developments in the field over time, spanning many centuries, from the very first recorded reflections on the nature of matter to the latest developments at the frontiers of lithography science and technology. Nonetheless, the emphasis is predominantly placed on applications that have relevance in the semiconductor industry. The enormous wealth of materials from which these illustrations and examples have been drawn means that this author’s choice is inherently peculiar, although each example is intended to provide deeper insight into the underlying principles involved.

A great many of the pioneers of chemistry and lithography are not represented herein at all. I can only record my immense debt to them and all who have contributed to the development of the two fields to the state in which I have reported it.

I am indebted to a number of people who in one way or another made this book possible. My academic mentor, the late Professor William C. Gardiner, Jr. of The University of Texas at Austin, distinguished teacher and physical chemist, himself the author of numerous books, introduced me to physical chemistry and guided my academic development in the field.

Professor C. Grant Willson of The University of Texas at Austin introduced me to lithography and supervised my doctoral thesis. I learned the intricacies of resist processing under the tutelage of the late Dr. Jeffrey Byers of SEMATECH.

A number of colleagues and associates proofread the entire manuscript or some chapters of the book, and provided valuable suggestions and corrections. These include Dr. Harry J. Levinson, my manager at AMD and also at GlobalFoundries, and Dr. Chris Mack, developer of PROLITH and founder of the FINLE Corporation, both of whom read the entire manuscript. Dr. Jim Thackeray of Rohm and Haas Electronic Materials read Chapters 5–8; these are the chapters dealing with lithographic chemicals. Dr. Witek Maszara of GlobalFoundries read Chapter 16, which deals with the application of lithography in IC device fabrication. These reviewers should not be blamed for any errors that may remain, which are strictly my responsibility.

In a less direct way, I have benefited throughout my professional career from scientific and technical discussions in the area of advanced lithography with colleagues at the strategic lithography technology departments of both AMD and GlobalFoundries, as well as at the lithography department of
IMEC (Inter-University Microelectronics Center). I have also benefited from scientific discussions in the area of polymers and photochemistry with Professor Katharina Al-Shamery of Univeristät Oldenburg in Germany, and in the area of physical methods of polymer characterization with Professors Jim Watkins and Todd Emrick of the University of Massachusetts at Amherst.

I also want to express my sincere thanks to the editorial staff of SPIE, and especially to Dara Burrows and Tim Lamkins, who have been most sympathetic and helpful at all times during the course of writing this book. They remained undismayed by the long delays as the length of the book expanded far beyond what we originally agreed to. The book is a much better book because of their editorial assistance.

Portions of this book were written in libraries and museums in a number of locations within the United States and Germany. I am particularly grateful to the staff of the archives of the Deutsches Museum in Munich, especially to Dr. Eva Mayring, Margrit Prussat, and Wolfgang Schinhan, for the assistance they rendered to me during my research at their facility in locating archival materials on and by some of the seminal individuals whose research in decades and centuries gone by greatly contributed to the invention and development of lithography.

The permission granted to me by AMD and extended by GlobalFoundries, the two companies for which I work, made it possible for me to write this book. I am indebted to Michela Jacob, the librarian in the AMD Fab30 facility and GlobalFoundries Fab1 in Dresden, Germany, for the numerous books and articles she was able to procure for me, sometimes from libraries far-flung from Dresden. I am also indebted to the individuals and publishers who granted me the permission to reproduce in this book some of their copyrighted figures and tables.

Finally, I must acknowledge the assistance I have received from my family members. Writing a book of this size takes undue toll on everyone directly or indirectly involved with it, particularly family members who have had to endure all kinds of inconveniences too numerous to mention. I wish therefore to acknowledge their helpful support. For these and other blessings, I am truly grateful.

Uzodinma Okoroanyanwu
Florence Village, Northampton, Massachusetts
November 2010
Acronyms and Abbreviations

AEE aminoethoxy ethanol
AFM atomic force microscope
AIBN azobis(isobutyronitrile)
AMC airborne molecular contaminant
APM atomic processing microscope
AR antireflection
ARC antireflection coating
att-PSM attenuated phase-shifting mask
BARC bottom antireflection coating
BEOL back end of line
BIM binary intensity masks
BJT bipolar junction transistor
BLR bilayer resist
BOCST butoxycarbonyloxystyrene
BOP benzyl-protected poly(p-hydroxystyrene)
BPO benzoyl peroxide
CaF$_2$ calcium fluoride
CAD computer-aided design
CAR chemically amplified resist
CARL chemical amplification of resist lines
CBN carbomethoxy norbornene
CD critical dimension
CFC chlorofluorocarbon
CH cyclohexanone
CMN carbomethoxy norbornene
CMOS complimentary metal-oxide semiconductor
CMP chemical mechanical polishing
CMTF critical modulation transfer function
CO cycloolefin
COG chromium-on-glass
COMA cycloolefin-maleic anhydride
COP crystal-originated pit
CPU central processing unit
CVD chemical vapor deposition
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>DEA</td>
<td>dissociative electron attachment</td>
</tr>
<tr>
<td>DEAP</td>
<td>diethoxyacetophenone</td>
</tr>
<tr>
<td>DMAc</td>
<td>dimethylacetamide</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMI</td>
<td>dimethyl-2-imidazolidinone</td>
</tr>
<tr>
<td>DMPA</td>
<td>dimethoxy phenylacetophenone</td>
</tr>
<tr>
<td>DMSDMA</td>
<td>dimethylsilyldimethylamine</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>DNQ</td>
<td>diazonaphthoquinone</td>
</tr>
<tr>
<td>DOF</td>
<td>depth of focus</td>
</tr>
<tr>
<td>DP</td>
<td>degree of polymerization</td>
</tr>
<tr>
<td>DPD</td>
<td>diazopyrazolidine dione</td>
</tr>
<tr>
<td>DPP</td>
<td>discharge-produced plasma</td>
</tr>
<tr>
<td>DPPH</td>
<td>diphenyl picrylhydrazyl</td>
</tr>
<tr>
<td>DRAM</td>
<td>dynamic random access memory</td>
</tr>
<tr>
<td>DRLS</td>
<td>development rate log slope</td>
</tr>
<tr>
<td>DRM</td>
<td>development rate monitor</td>
</tr>
<tr>
<td>DTBP</td>
<td>di-tert-butyl peroxide</td>
</tr>
<tr>
<td>DTBPIONf</td>
<td>di(tert-butyphlenyl) iodonium perfluorobutanesulfonate (nonaflate)</td>
</tr>
<tr>
<td>DUV</td>
<td>deep ultraviolet</td>
</tr>
<tr>
<td>EBES</td>
<td>electron-beam exposure system</td>
</tr>
<tr>
<td>EBL</td>
<td>electron-beam lithography</td>
</tr>
<tr>
<td>ECR</td>
<td>electron cyclotron resonance</td>
</tr>
<tr>
<td>EFM</td>
<td>electric-field-induced migration</td>
</tr>
<tr>
<td>EL</td>
<td>ethyl lactate</td>
</tr>
<tr>
<td>EOC</td>
<td>etalon output coupler</td>
</tr>
<tr>
<td>EOL</td>
<td>end of line</td>
</tr>
<tr>
<td>EPR</td>
<td>electron projection lithography</td>
</tr>
<tr>
<td>ESCAP</td>
<td>environmentally stable chemically amplified photoresist</td>
</tr>
<tr>
<td>ESD</td>
<td>electrostatic discharge</td>
</tr>
<tr>
<td>EUV</td>
<td>extreme ultraviolet</td>
</tr>
<tr>
<td>FEOL</td>
<td>front end of line</td>
</tr>
<tr>
<td>FET</td>
<td>field-effect transistor</td>
</tr>
<tr>
<td>FIB</td>
<td>focused ion beam</td>
</tr>
<tr>
<td>FRP</td>
<td>free radical polymerization</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width half maximum</td>
</tr>
<tr>
<td>HDPCVD</td>
<td>high-density chemical vapor deposition</td>
</tr>
<tr>
<td>HEPA</td>
<td>high-efficiency particulate air</td>
</tr>
<tr>
<td>HF</td>
<td>hydrofluoric acid</td>
</tr>
<tr>
<td>HMDS</td>
<td>hexamethyldisilazane</td>
</tr>
<tr>
<td>HOL</td>
<td>hydrophilic overlayer</td>
</tr>
<tr>
<td>HSQ</td>
<td>hydrogen silesquioxanes</td>
</tr>
</tbody>
</table>
HVM | high-volume manufacturing  
IC | integrated circuit  
IGFET | insulated gate field-effect transistor  
ILD | interlayer dielectric  
IMS | ion microfabrication system  
IPL | ion projection lithography  
ITRS | International Roadmap for Semiconductors  
JFET | junction field-effect transistor  
KRS | ketal resist system  
KTFR | Kodak Thin Film™ resist  
LBNL | Lawrence Berkeley National Laboratories  
LEE | low-energy electron  
LEEPL | low-energy electron projection lithography  
LELE | lithography-etch-lithography-etch  
LER | line edge roughness  
LFLE | lithography-freeze-lithography-etch  
LLD | lightly doped drain  
LPCVD | low-pressure chemical vapor deposition  
LPP | laser-produced plasma  
L/S | line/space  
LWR | line width roughness  
Mac | methylacetamide  
MEA | monoethanolamine  
MEBES | multiple electron-beam exposure system  
MEEF | mask error enhancement factor  
MEMS | microelectromechanical system  
MET | microexposure tool  
MIBK | methylisobutyl ketone  
MIF | metal-ion-free  
ML | multilayer  
MMA | methyl methacrylate  
MOCVD | metal-organic chemical vapor deposition  
MOP | methoxypropyl-protected poly(p-hydroxy styrene)  
MOS | metal-oxide semiconductor  
MOSFET | metal-oxide semiconductor field-effect transistor  
MTF | modulation transfer function  
MW | molecular weight  
NA | numerical aperture  
NBHFA | norbornene hexafluoroisopropanol  
NHA | numerical half-aperture  
NH₄HF | ammonium fluoride  
NILS | normalized image log-slope  
nMOS | n-channel metal-oxide semiconductor  
NMP | N-methylpyrrolidone  
NVSM | nonvolatile semiconductor memory
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>OPC</td>
<td>optical proximity correction</td>
</tr>
<tr>
<td>OPD</td>
<td>optical path difference</td>
</tr>
<tr>
<td>OPE</td>
<td>optical proximity effect</td>
</tr>
<tr>
<td>PAC</td>
<td>photoactive compound</td>
</tr>
<tr>
<td>PAG</td>
<td>photoacid generator</td>
</tr>
<tr>
<td>PBOCST</td>
<td>poly(tert-butoxycarbonyl oxy styrene)</td>
</tr>
<tr>
<td>PBS</td>
<td>poly(butene sulfone)</td>
</tr>
<tr>
<td>PCB</td>
<td>printed circuit board</td>
</tr>
<tr>
<td>PCM</td>
<td>portable conformable mask</td>
</tr>
<tr>
<td>PDMS</td>
<td>polydimethylsiloxane</td>
</tr>
<tr>
<td>PE</td>
<td>photoelectron</td>
</tr>
<tr>
<td>PEB</td>
<td>postexposure bake</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma-enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>PFOS</td>
<td>perfluorooctane sulfonic acid</td>
</tr>
<tr>
<td>PGMA</td>
<td>poly(glycidyl methacrylate)</td>
</tr>
<tr>
<td>PGME</td>
<td>propylene glycol monomethylether</td>
</tr>
<tr>
<td>PGMEA</td>
<td>propyleneglycol monomethyl ether acetate</td>
</tr>
<tr>
<td>PHOST</td>
<td>polyhydroxystyrene</td>
</tr>
<tr>
<td>PMIPK</td>
<td>poly(methyl isopropenyl ketone)</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>pMOS</td>
<td>$p$-channel metal-oxide semiconductor (field-effect transistor)</td>
</tr>
<tr>
<td>PMPS</td>
<td>poly(methylpentene sulfone)</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>PPDA</td>
<td>$p$-phenylenediacylic acid</td>
</tr>
<tr>
<td>PREVAIL</td>
<td>projection reduction exposure with variable axis immersion lens</td>
</tr>
<tr>
<td>PROLITH</td>
<td>positive resist optical lithography</td>
</tr>
<tr>
<td>PSM</td>
<td>phase-shifting mask</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>PVP</td>
<td>poly(vinyl pyridine)</td>
</tr>
<tr>
<td>PWB</td>
<td>printed wiring board</td>
</tr>
<tr>
<td>RB</td>
<td>rose bengal</td>
</tr>
<tr>
<td>RC</td>
<td>resistance capacitance</td>
</tr>
<tr>
<td>RELACS</td>
<td>resolution enhancement of lithography assisted by chemical shrink</td>
</tr>
<tr>
<td>RIE</td>
<td>reactive-ion etching</td>
</tr>
<tr>
<td>ROMP</td>
<td>ring-opening metathesis polymerization</td>
</tr>
<tr>
<td>SADP</td>
<td>self-aligned double patterning</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
</tr>
<tr>
<td>SCALPEL</td>
<td>scattering with angular limitation projection electron-beam lithography</td>
</tr>
<tr>
<td>S/D</td>
<td>source/drain</td>
</tr>
<tr>
<td>SEMC</td>
<td>single-electron memory cell</td>
</tr>
<tr>
<td>SLM</td>
<td>spatial light modulator</td>
</tr>
<tr>
<td>SLR</td>
<td>single-layer resist</td>
</tr>
<tr>
<td>SNS</td>
<td>sulfone/novolak system</td>
</tr>
</tbody>
</table>
SPM  sulfuric acid and hydrogen peroxide mixture
STI  shallow trench isolation
STM  scanning tunneling microscope
TBEST tert-butyl ester-protected 4-hydroxystyrene
TBMA tert-butyl methacrylate
TBTTFMA tert-butyl-2-trifluoromethylacrylate
TCAD technology computer-aided design
TE  transverse electric
TEM  transmission electron microscopy
TFE  tetrafluoroethylene
THF  tetrahydrofuran
THP  tetrapyrnal
TM  transverse magnetic
TMAH  tetramethylammonium hydroxide
TMS  trimethylsilyl
TMSDEA trimethylsilyldiethylamine
TMSDMA trimethylsilyldimethylamine
TPSHFA triphenylsulfonium hexafluoroantimonate
TSI  top surface imaging
ULPA ultralow-penetration air
UTR  ultrathin resist
UV  ultraviolet
VAP  vinyl addition polymerization
VEMA poly(vinyl ether-alt-maleic anhydride)
VUV  vacuum ultraviolet
WET  wafer electrical test
XRR  x-ray reflectivity