

Chemistry and Lithography

Vol. I: The Chemical History of Lithography

SECOND EDITION

Uzodinma Okoroanyanwu

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General Preface to the Second Edition

A second edition of a text has a number of advantages over the first edition: in addition to representing the accumulated wisdom of the readers who have suggested ideas for improving the previous edition, it also incorporates developments in the field that have taken place since the publication of the first edition. From their familiarity with the previous edition and in keeping with the general aim to make the text accessible, readers will be aware that I have provided not a slight tinkering with the text in this edition, but a wholesale rewriting of some chapters, while introducing entirely many new ones.

This present edition is a series of three volumes, namely, *The Chemical History of Lithography* (volume 1), *Chemistry in Lithography* (volume 2), and *The Practice of Lithography* (volume 3). Each volume is a unit in itself and can stand alone, which is fortunate in view of their different subject matters.

My motivation for splitting the second edition of *Chemistry and Lithography* into the above three volumes is because the subject matter of these three books is very broad and lends itself nicely to multiple angles of analysis and interpretation. Lithographically fabricated structures appear in an increasing wide range of scientific and technical fields, beyond their traditional niches in fine arts, paper printing, and electronics. In particular, the last ten years since the publication of the first edition of *Chemistry and Lithography* have witnessed a phenomenal pace of development in advanced lithography, perhaps the fastest pace of development in any decade over the 222-year history of the field. The transistor count of the leading-edge integrated circuit when the first edition was published was around 2.5 billion, and a short five years later that count rose to 10 billion. By the time the present edition is published, the transistor count of an equivalent device may well be over 20 billion, representing a nearly ten-fold increase within a decade in the ability to process, communicate, and store electronic information, made possible in no small part by advances in lithography. Such is the pace of the development in this field that the analysis I make in these three volumes is a sufficiently different and significantly expanded version of the treatment of the

subject I rendered in the first edition. As such, there are a considerable number of changes within the text of the present edition.

The first edition covered some brief historical material in Part I, and in volume 1 of the present edition these historical aspects are extended. It seems reasonable to me that with the rapid advances being made in advanced lithography it is very important to realize that some of the concepts that we now take for granted in chemistry and physics that enervate lithography are by no means self-evident and often were developed only after much struggle and controversy. Improvements are still being made in all of these fields and can all the more be clearly understood by those who appreciate how our present understanding of the fields were attained.

In developing volume 1 of the present edition, I drew considerably from Part I of the first edition. Relative to Part I of the first edition, volume 1 of the present edition comprises five significantly expanded chapters: Chapters 1 and 2 of first edition with slight tinkering; an expanded version of Chapter 4 of the first edition; and two new chapters derived from expanding and splitting up Chapter 3 of the first edition. The object of volume 1 of the present edition is to weave together threads of a narrative on the history of optical and molecular physics, optical technology, chemistry, and lithography, with a view to creating a rich tapestry that gives the reader new insights into an aspect of the relationships between these fields that are often not fully appreciated: how the marriage between chemistry and optics led to the development and evolution of lithography. I show how major developments in the chemistry, physics, and technology of light influenced the invention and development of lithography, well beyond what its inventor envisioned. I also show how developments in lithography have not only influenced the development of optics and chemistry, but also played a critical role in the large-scale manufacture of integrated circuits that run the computers and machineries on which our modern electronic and information age depend.

Part of the analysis in volume 1 of the present edition is necessarily skewed toward the underlying science and technologies of advanced lithographic patterning techniques, in terms of materials, processes, and imaging, along with their unique features, strengths, and limitations. This book also provides an analysis of the emerging trends in lithographic patterning, as well as the current and potential applications of the resulting patterned structures and surfaces.

The object of volume 2 of the present edition is to deconstruct lithography into its essential chemical principles and to situate its various aspects in specific fields of chemistry. It comprises 16 chapters developed around a rewriting of Chapters 5 through 8 of Part II of the first edition and parts of Chapters 13 and 14 of Part III of the first edition. It also includes eight entirely new chapters that explore in a fundamental manner the role of chemistry in mediating specific aspects of the lithographic process.

Volume 2 of the present edition is in fact an outgrowth of the SPIE Advanced Lithography Short course Chemistry and Lithography (SC1099) that I have taught at the SPIE Advanced Lithography Symposium over the past six years. In this volume, I develop a chemistry and lithography interaction matrix, and use it as a device to illustrate how various aspects and practices of advanced lithography derive from established principles and phenomena of chemistry. For instance, lithographic unit operations involving principally the resist fall within the realm of process chemistry. Photochemistry is involved in the generation of photons from the exposure sources of optical, extreme ultraviolet, and x-ray lithographic exposure tools; the interaction of O_2 , H_2O , NH_3 , SO_x , and hydrocarbons with photons within the optical lithographic tool exposure chamber, as well as their roles in the oxidation, carbon deposition and growth, and formation of inorganic salt crystals (also called haze crystals) on masks and optical elements; cleaning of contaminated optics and masks with UV photons; clear defect repair of masks via photo-induced decomposition of organometallic precursors and deposition of metals on defective areas of the mask; and UV curing and photo-oxidative degradations of resists during exposure. Photochemistry is also the basis of the exposure action of photoacids and photobases in resists, as well as resist poisoning by airborne molecular bases. It is also the basis of laser-produced and discharge produced plasmas—the radiation sources for extreme-ultraviolet (EUV) lithographic patterning. Finally, photochemistry is the basis of the plasma (dry) stripping of resists and other hydrocarbon contaminants from wafers and masks.

Similarly, radiation chemistry is involved in the generation of electrons and ions from the exposure sources of electron-beam and ion-beam lithographic exposure tools, respectively; cleaning of contaminated optics and masks, and repair of defective masks with electrons and ions; the electron- and ion-mediated exposure process as well as electron-beam and ion-beam curing, and crosslinking of resists. The manufacture of lithographic exposure sources, optical elements, masks, and resist materials involves materials chemistry. Polymer chemistry is the basis of the synthesis of polymeric resist resins used in optical, charged particle, and imprint lithography, as well as block copolymers used in directed block copolymer self-assembly lithography.

Surface chemistry is the basis of priming of relevant mask and wafer substrates, and their subsequent coating with resists and associated layers used in the fabrication of masks and semiconductor device wafers. Colloid chemistry is the basis of the cleaning of masks and wafers, and development process of exposed resists. It also explains the basis for the stability of resist, developer, and wet cleaning solutions. Electrochemistry is the basis of the corrosion and electromigration processes of Cr and Mo mask or reticle absorber features, as well as electrostatic damage of the same objects. It is also the basis of electrochemical imprint lithography. Organometallic chemistry is

the basis for the precursor materials used in clear defect repair of masks, as well as EUV metal-oxide resists.

The Practice of Lithography (volume 3) comprises 12 chapters, made up of Chapters 9 through 17 of the first edition, in addition to three new chapters covering full treatment of EUV lithography, as well as imprint lithography, directed block copolymer self-assembly lithography, and proximal probe lithography. The object of this volume is to present how the more important lithographic patterning techniques are used to print images on appropriately prepared flat substrate surfaces using radiations as varied as photons, electrons, and ions, as well as mechanical force, thermodynamically driven directed self-assembly of block copolymers, and even electron tunneling phenomena. In particular, I cover photolithography (or optical lithography), electron-beam lithography, ion-beam lithography, EUV lithography, imprint lithography, directed block copolymer self-assembly lithography, and proximal probe lithography.

Immersion ArF laser optical lithography is currently used in high-volume manufacture of integrated circuits at 22-, 15-, and 10-nm nodes, using double-patterning techniques to decrease feature pitch, where appropriate. EUV lithography is now entering high-volume production at the 7-nm node in some of the leading-edge semiconductor companies. Imprint lithography, especially in its roll-to-roll format, is increasingly being used in the fabrication of flexible and wearable electronic devices, diffractive optical elements, and large-area electronics. Directed block copolymer self-assembly is increasingly being used in the fabrication of functional nanostructures used in applications ranging from photonics to biomimetics, and from electrochemical energy storage to patterned electronic media. Now is an auspicious moment to provide an in-depth look into the chemistry that underpins these most advanced of lithographies.

Along with the introduction of EUV lithography into device manufacturing at single-digit-nanometer technology nodes, we enter a regime where the resist suffers from increased stochastic variation and the attendant effects of shot noise—a consequence of the discrete nature of photons, which, at very low number per exposure pixel, show increased variability in the response of the resist relative to its mean. Examples of resist response that may experience shot noise effects under very low-photon-count-per-pixel conditions within small exposure volumes, such as in EUV lithographic patterning, include photon absorption by the resist, and chemical conversion of light sensitive components in the resist, as well as the chemical changes that make a resist molecule soluble in the developer. We will examine in this volume of the present edition the role of stochastics in EUV lithography in far greater detail than we did in the first edition.

As in the first edition, I have made an attempt throughout the three books of the present edition to provide examples illustrating the diversity of chemical phenomena in lithography across the breadth of scientific spectrum, from

fundamental research to technological applications. The format of this book is not necessarily chronological, but it 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 currently at the frontiers of lithography science and technology. The emphasis is mostly placed on applications that have relevance to the semiconductor industry.

A great many of the pioneers of chemistry and lithography are not represented at all in the three books of the present edition. 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 most grateful for suggestions from a number of experts, particularly the following: Andreas Erdman of Fraunhofer IISB, Manuel Thesen of micro resist technology GmbH, and Folarin Latinwo of Synopsys. Special thanks go to SPIE Senior Editor, Dara Burrows, for her editorial assistance in producing this book, which is much improved because of her efforts.

I am also grateful to my colleagues in the Department of Polymer Science and Engineering of University of Massachusetts at Amherst and, in particular, Prof. Jim Watkins, for lively scientific and technical discussions on polymers and flexible electronics. The opportunity to work in this department has not only helped me to broaden and deepen my scientific research interests, but also, in a direct way, has made it possible for me to write this book.

Lastly, I acknowledge the informal assistance I have received from my family members, in particular, from my wife Anett and daughter Sophie, who created a conducive atmosphere to work on this book at home.

Uzodinma Okoroanyanwu

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January 2020

Chapter 4

Chemical Origins of Lithography

“It is the great beauty of our science, chemistry, that advancement in it, whether in a degree great or small, instead of exhausting the subjects of research, opens the doors to further and more abundant knowledge, overflowing with beauty and utility to those who will be at the easy personal pains of undertaking its experimental investigation.”¹

Michael Faraday (1791–1867)

4.1 Introduction

In order to arrive at a fuller understanding of lithography, it is necessary to examine the work of a large number of scientists whose contributions to chemistry, spanning a period of over 3000 years, were instrumental in shaping the invention of lithography in 1798 by Senefelder² and its subsequent development, evolution, and progress. This story not only relates a triumph of advances in the understanding of materials science, but is also a product of the knowledge gained in the convergence of major areas of chemistry and physics (particularly those related to optical, atomic, and molecular physics, which are covered in Chapter 3). Our object here thus is to consider how key theoretical and technological developments in chemistry have influenced the development of lithography.

It is also imperative that we examine ways of overcoming the challenges presented by ever-more-demanding applications of sophisticated chemistry in semiconductor lithography, in terms of materials, processes, and tools.

¹M. Faraday, “On electro-chemical decomposition,” *LX. Experimental Researches in Electricity, 7th Ser., The Annals of Electricity, Magnetism and Chemistry and Guardian of Experimental Science*, p. 366 (1837).

²A. Senefelder, *Vollständiges Lehrbuch der Steindruckerei [A Complete Course in Lithography, in German]*, Karl Thienemann, Munich and Karl Gerold, Vienna, Publishers (1818).

In 1877 van't Hoff replaced the indefinite “force” by velocity of reaction. The velocity with which A and B react to form A' and B' he expressed as $v' = kpq$, and the velocity with which A' and B' react to form A and B he expressed as $v' = k' p' q'$. The actual velocity of the complete reaction is therefore given by $V = v - v' = kpq - k' p' q'$. At equilibrium, $V = 0$, and $p' q' / pq = k/k'$.¹⁵⁸

Kinetics, the branch of physical chemistry dealing with rates of chemical reactions, therefore had its origins in the above-mentioned works of Guldberg and Waage as well as that of van't Hoff. Today, the techniques developed by these scientists are used to study rates of various reactions involved in lithographic patterning. A few examples of these lithographic reactions include deprotection kinetics of chemical amplification resists, development kinetics of resists, kinetics of photolysis of photoacid generators in chemical amplification resists, and color center formation in quartz glass of lithographic exposure tools, to mentioned but a few.

4.3.10 Thermochemical laws

The foundations of the branch of physical chemistry dealing with thermochemistry was laid by Lavoisier and Laplace, who through their collaborative efforts showed that the heat evolved in a reaction equals the heat absorbed in the reverse reaction. They investigated the specific and latent heats of a number of substances, as well as the amount of heat generated in combustion. It was Germain Henri Hess (1802–1850) who in 1840 enunciated the law that now bears his name—Hess' law:¹⁵⁹ The evolution of heat in a reaction is the same whether the process is accomplished in one step or in a number of stages. As an illustration, the heat from the formation of CO_2 is the sum of the heat from the formation of CO and the heat from the oxidation of CO to CO_2 .¹⁶⁰

When the mechanical theory of heat was enunciated, Hess' law was soon realized to be a consequence of the law of conservation of energy, which states that energy cannot be created nor destroyed, but can be transformed from one form to another. A consideration of the second law of thermodynamics, enunciated by Nicolas Léonard Sadi Carnot (1796–1832) in 1824, influenced Hermann von Helmholtz (1821–1894) in 1882 to estimate the work done by the chemical forces not as the heat evolved in the reaction, but as the largest quantity of work that can be gained when the reaction is carried out in a reversible manner, e.g., electrical work in a reversible cell. This maximum work is regarded as the diminution of the free or available energy of the

¹⁵⁸ibid., p. 327.

¹⁵⁹H. Hess, “Thermochemische Untersuchungen,” *Ann. Physik.* **50**, 385–404 (1840); *Ostwald's Klassiker* No. 9 [cited in J.R. Partington, *A Short History of Chemistry*, 3rd ed., Dover Publications, New York, pp. 327–328 (1989)].

¹⁶⁰ibid., p. 327.

system, while the heat evolved is regarded as a measure of the diminution of the total energy of the system.¹⁶¹

The application of the second law of thermodynamics to chemistry, first occurring notably in the study of dissociation phenomena in solids, influenced Henry John Horstman (1854–1929) in 1873 to point out that such changes are similar to physical changes of state, and that the thermodynamic equation derived by Benoît Paul Émile Clapeyron (1799–1864) and Rudolf Clausius (1822–1888) for changes of state are also applicable here, i.e., $dp/dT = Q/T(v' - v)$, where p is the dissociation pressure, Q is the heat of dissociation, T is the absolute temperature, and v' and v are the volumes of the system after and before dissociation, respectively. In the case in which a gas or vapor formed is supposed to behave as an ideal gas, and the volume of the solids is neglected in comparison with that of the gas, the equation becomes $d \log p/dT = Q/RT^2$, where R is the universal gas constant.¹⁶²

Between 1884 and 1886, van't Hoff generalized this equation to make it applicable to all cases of chemical equilibrium between gases or substances in dilute solution. To this end, he replaced p with the equilibrium constant K in the above equation.¹⁶³ However, although the integration of this equation gives a means of finding Q from measurements of the effect of temperature on K , it does not solve the problem of calculating K from the heat of reaction Q since the equation contains an unknown constant of integration: $\log K = -Q/RT + \text{constant}$. It was in 1906 that Walther Nernst (1864–1941) showed that by making another assumption it was possible to calculate the value of this constant, and the problem of finding K and hence the affinity from the heat of reaction was solved.¹⁶⁴

4.3.11 The phase rule

The phase rule enunciated by Josiah Willard Gibbs (1839–1903) in 1876 is the most useful guide for predicting equilibrium in systems that are not homogeneous. The rule deals with systems containing more than two different bodies, called *phases*, which are separated by boundaries, e.g., liquid and gas, or liquid and solid. Such a system can be built up from a certain minimum number of chemical substances called *components*. In order for a system to be in equilibrium, Gibbs asserts, certain conditions of temperature, pressure, and the concentrations in the various phases must be satisfied. He called the number of these variables, which must be fixed before there is equilibrium,

¹⁶¹*Ostwald's Klassiker* No. 124 [cited in J.R. Partington, *A Short History of Chemistry*, 3rd ed., Dover Publications, New York, p. 328 (1989)].

¹⁶²J.R. Partington, *A Short History of Chemistry*, 3rd ed., Dover Publications, New York, pp. 328–329 (1989).

¹⁶³*ibid.*, p. 329.

¹⁶⁴*ibid.*, p. 329.

Chapter 5

Evolution of Lithography

“The old order changeth, yielding place to new.”

Alfred Tennyson (1809–1892), *The Idylls of the King*

5.1 Introduction

From the time of Senefelder to the present, lithography has undergone tremendous evolution, but overall, its basic principle remains intact. It remains a planographic printing process in which the image and nonimage areas are on the same plane of the printing substrate.¹ Just as in Senefelder’s time, today, the contrast between the image and nonimage areas depends on the interfacial tension of oily inks and water-retaining surfaces. This is in fact the very same principle that governs the immiscibility of oil and water—hydrophobic–hydrophilic interactions between the image and nonimage areas. The inks (or resist) are naturally hydrophobic and can be made resistant to the action of etchants when dry.

Lithography has evolved into a broad family of techniques that are distinctly different in many respects, yet share similar attributes as to their ultimate goal—a method to transfer information from one substrate to another with a high degree of fidelity and throughput relative to other comparable printing techniques. Senefelder’s original direct stone plate lithography of the late 18th century evolved into offset lithography in the 19th century and is now primarily used in the printing industry. Offset lithography in turn evolved into semiconductor lithography in the 20th century, where it is now used in the fabrication of ICs. Many variants of lithography are currently practiced, ranging from stone plate lithography used in fine art printing, to offset lithography used in the printing of newspapers and the like, to semiconductor lithography that utilizes a variety of exposure radiations to print ICs, to emerging lithographies based on molecular self-assembly, imprinting or

¹Lithography is one of the three basic printing methods, the other two being intaglio (gravure or engraving) and typography (relief printing).

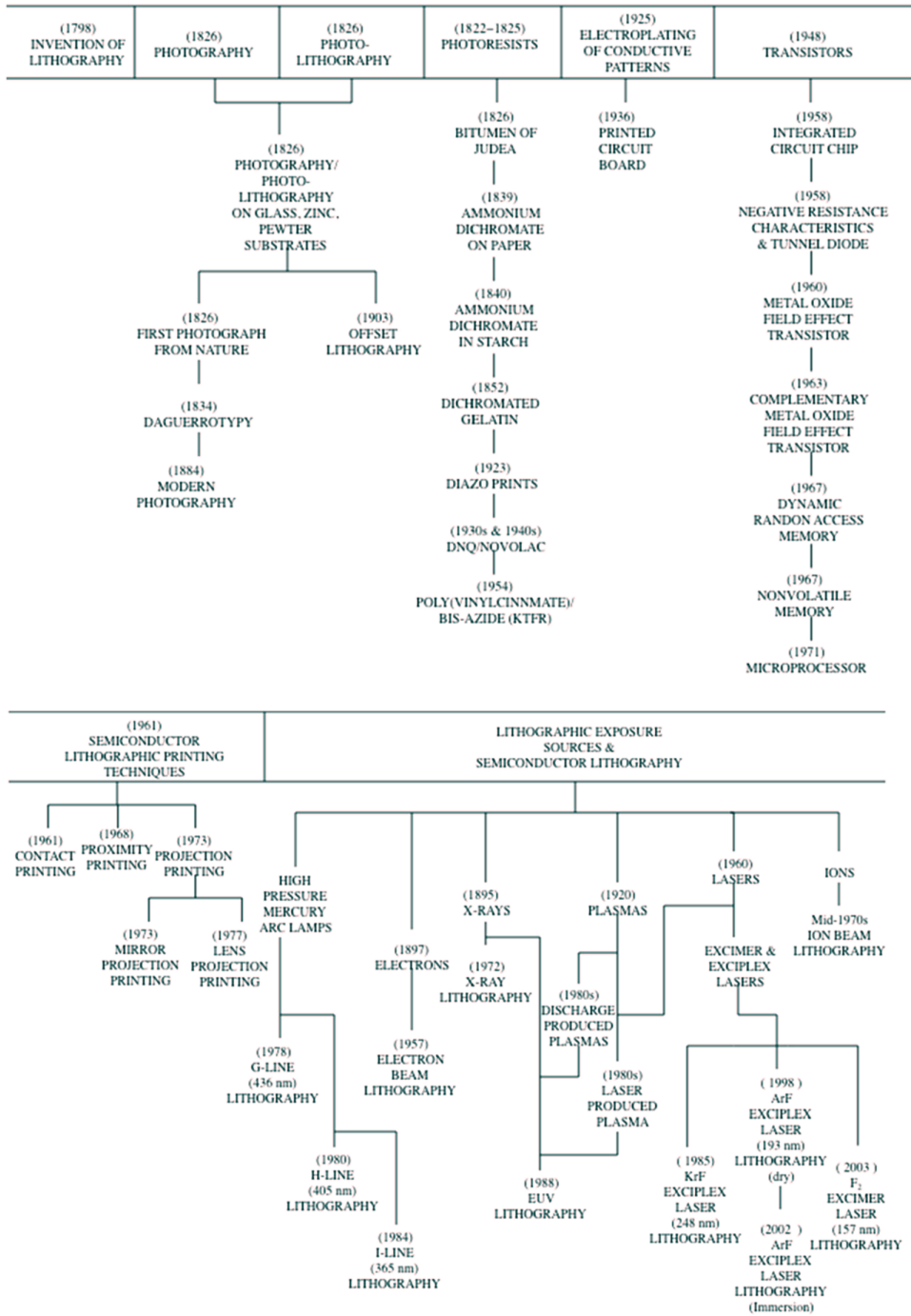


Figure 5.1 Evolution of lithography.

various materials using computer-to-plate technology. In addition to digital information from computers, film positives and negatives are used in making or exposing most types of offset plates today. While there are several types of offset plates, they are all generally classified as either positive or negative working plates, depending on the tone of their printing.⁴⁵

The ink used in offset lithography has properties similar to those used in a letterpress in that both inks are very viscous. The water solution, called a “fountain solution,” is used to keep the ink from adhering to the non-image areas of the offset plate. The fountain solution is formulated from materials such as desensitizing gums, cleaners, buffering agents, etc.⁴⁶ Offset lithographic printing is the dominant printing method used in the printing of newspapers, textbooks, and the like.

5.3 The Printed Circuit Board and the Development of the Electronics Industry

Printed circuit boards are in almost all electronics and computerized devices that make our modern world possible. They are the essential framework on which electronic components are assembled and integrated to make functional devices. The printed circuit board (PCB)⁴⁷ and modern resist technologies are both outgrowths of the printing industry, whereas resists had been known for more than a century before the invention of the PCB. In early PCB processes, etch resists were applied by offset lithographic printing, resulting inevitably in the transfer of printing technologies to the PCB industry.⁴⁸ To better understand the role that lithography, specifically offset lithography, played in the development of PCB, a brief discussion on the invention and development of PCBs is presented.

The roots of PCBs stretch all the way back to 1903, when the German scientist Albert Hanson filed a British patent⁴⁹ for a device meant to improve telephone exchange boards. His simple device was made using through-hole construction, which allowed conductor wires to be passed through the holes in the substrate to be soldered or bonded to copper or brass traces on the flat surface of the substrate. The traces were adhesively bonded to the substrate (paraffined paper and the like). Although Hanson’s device was not a truly *printed* circuit board, as the conductor metal patterns were either cut or stamped out, it did produce conductive metal patterns on a dielectric

⁴⁵ibid.

⁴⁶ibid.

⁴⁷The account rendered here is adapted from a similar one given in W.S. DeForest, *Photoresist: Materials and Processes*, McGraw-Hill, New York, Chapter 1 (1975).

⁴⁸ibid., p. 6.

⁴⁹A. Hanson, “Improvements in or connected with electrical cables and jointing of the same,” British Patent 4,681 (1903).

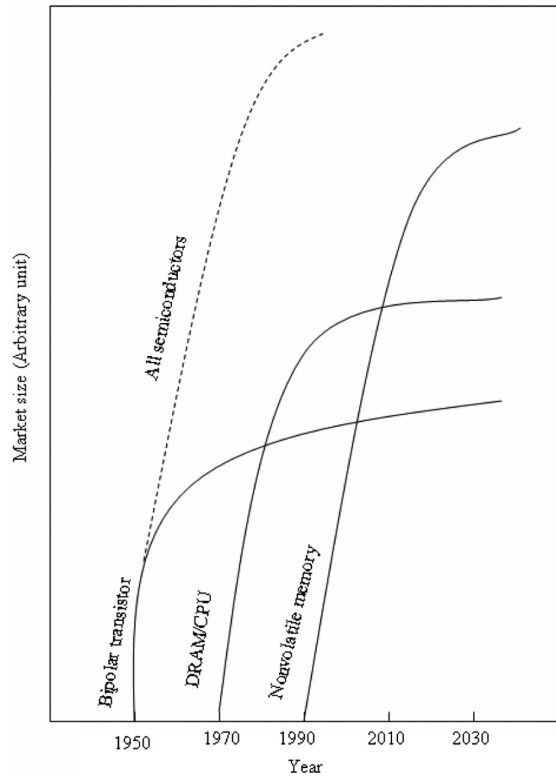


Figure 5.3 Growth curves for different IC devices that have been technology drivers over the years (plot generated in the manner of Masuoka¹²⁰).

The fact that demand for memory has continued to be an important driving force within the IC industry over the last 50 years and is expected to remain so for the foreseeable future is a testament to the heightened sensitivity of these devices to yield factors. Yield depends significantly on the surface area of the device and is often negatively impacted by contaminants—either from particulates outside the process equipment or generated by the process equipment, or redeposits of process materials during processing. For this reason, yield is heavily affected by packing density, which in turn is a most apparent restriction in memory devices, making memory devices the technology drivers in the IC industry.¹²¹ Memory devices lead the industry in both device density and linewidth.¹²² Packing density is determined by linewidth, so any increases in memory size require smaller linewidths or larger

¹²⁰F. Masuoka, “Flash memory technology,” *Proc. Int. Electron Devices Mater. Symp.* **83**, Hsinchu, Taiwan (1996).

¹²¹VLSI Research Inc., “Wafer Fab Fabrication Equipment,” Report 2233-11P (1989).

¹²²*ibid.*

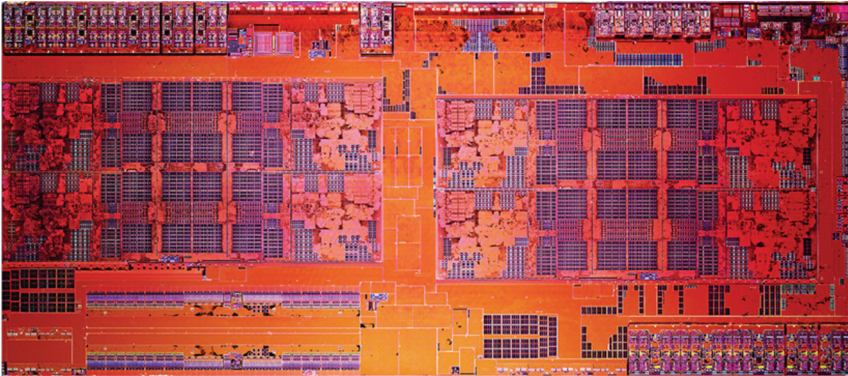


Figure 5.4 AMD’s Zen+™ microprocessor chip with up to 32 cores. Manufactured with a 12-nm technology node process, it has critical dimension of 12 nm, 12 metal layers, 4.8 billion transistors, and a silicon die size of 212.97 mm². The 32 cores are separate processors that act in parallel.¹²⁸

they are turning to multicore systems only because the path to higher clock speeds seems to be very difficult, at least for now.¹²⁹

The causes of this impasse derive from the peculiar physical and economic laws that govern the design of ICs.¹³⁰ The most celebrated of these laws stipulates that, as transistors or other components are made smaller and packed more densely on the surface of a silicon chip, the cost of producing the chip remains nearly constant, so much so that the number of transistors on a state-of-the-art chip doubles every year or two, as already alluded to. In effect, the cost per transistor steadily declines over time. This extraordinary fact is the basis of Moore’s law,¹³¹ formulated in 1965 by Gordon E. Moore, one of the founders of Intel Corporation. The law reflects the fantastic progression of circuit fabrication, which has unleashed previously unimagined computational power.¹³²

Less famous than Moore’s law but equally influential are several “scaling laws,” first formulated in 1974 by Robert H. Dennard and co-workers¹³³ at IBM, who asked: When the size of a transistor is reduced, how should the other factors such as voltages and currents that control its operation be adjusted? And what effect will the changes have on performance? Dennard and co-workers found that voltage and current should be proportional to the

¹²⁸<https://en.wikichip.org/wiki/amd/microarchitectures/zen%2B>.

¹²⁹ibid.

¹³⁰ibid.

¹³¹See, e.g., D.C. Brock, Ed., *Understanding Moore’s Law: Four Decades of Innovation*, Chemical Heritage Press, Philadelphia (2006).

¹³²See Fig. 1.1 in Chapter 1.

¹³³R. Dennard, F. Gaensslen, H.-N. Yu, V.L. Rideout, E. Bassous, and M. LeBlanc, “Design of ion-implanted MOSFETs with very small physical dimensions,” *IEEE J. Solid State Circuits* SC-9(5), 256–268 (1974).

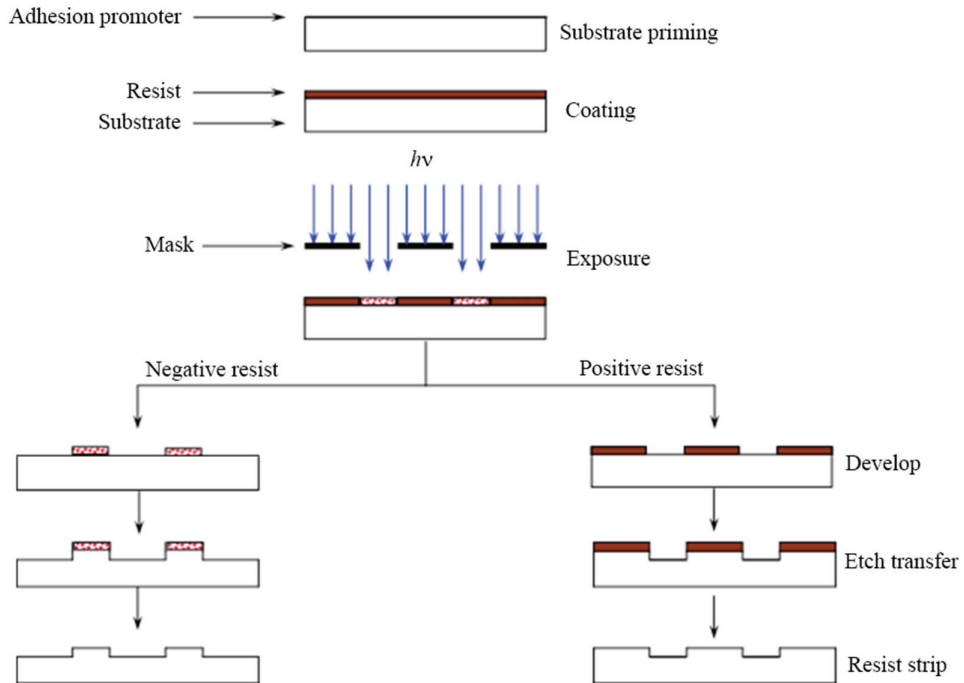


Figure 5.5 Schematic representation of the photolithographic process sequence.

film is developed in a solvent to produce a 3D relief replica of the mask pattern. Finally, the image in the resist is etched into the underlying substrate by liquid-based substrate etching systems or a variety of plasma (dry) etch processes.¹⁵² And at the end of the process, the remaining resist is stripped off, leaving the patterned features on the semiconductor substrate, which then undergoes subsequent processing to transform it into an actual IC device.

The two fundamental relationships describing optical lithographic resolution R and depth of focus (DOF) are given by

$$R = k_1 \frac{\lambda}{\text{NA}}, \quad (5.1)$$

$$\text{DOF} = k_2 \frac{\lambda}{(\text{NA})^2}, \quad (5.2)$$

where λ is the wavelength of the imaging radiation, and NA is the numerical aperture of the imaging system. The parameters k_1 and k_2 are empirically

¹⁵²G.M. Whitesides and J.C. Love, "The art of building small," *Scientific American Reports* **17**(3), 13–21 (2007); W.M. Moreau, *Semiconductor Lithography: Principles, Practices, and Materials*, Plenum, New York (1988); L.F. Thompson, C.G. Willson, and M.J. Bowden, Eds., *Introduction to Microlithography*, 2nd ed., American Chemical Society, Washington, D.C. (1994).

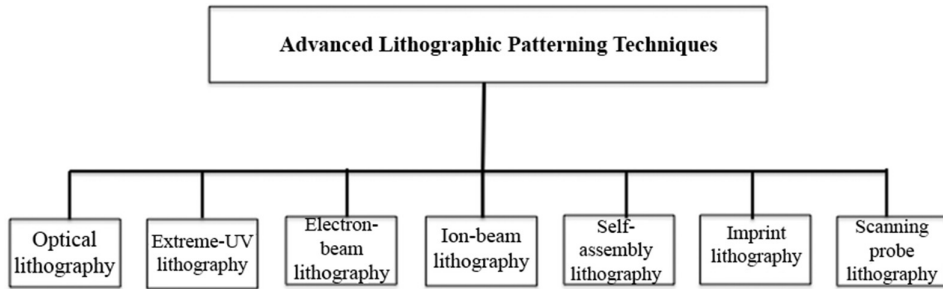


Figure 5.6 Advanced lithographic patterning techniques.

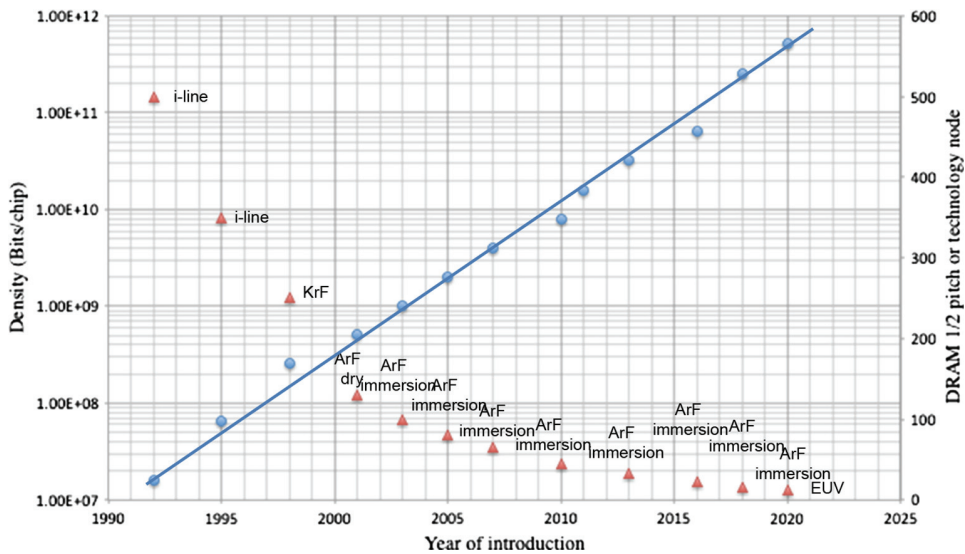


Figure 5.7 Evolution of semiconductor lithography as reflected in the exponential increase of dynamic random access memory (DRAM) density versus year of introduction, based on the 1999, 2011, and 2012 Semiconductor Industry Association Roadmap for Semiconductors.

Since its introduction, photolithography has undergone many innovations and evolutions,¹⁵⁶ as shown in Fig. 5.7 and Table 5.1.

The oldest photolithographic technique is contact printing,¹⁵⁷ whereby the mask is placed close to the wafer surface and is visually aligned to the previous pattern on the wafer in a process called registration and alignment. The mask is then pressed into hard contact with the resist-coated wafer, following which

¹⁵⁶An excellent account on developments in optical lithography between 1967 and 2007 is provided in J.H. Bruning, “Optical lithography: 40 years and holding,” *Proc. SPIE* **6520**, 652004 (2007) [doi: 10.1117/12.720631].

¹⁵⁷W.M. Moreau, *Semiconductor Lithography: Principles, Practices, and Materials*, Plenum, New York (1988); W.S. DeForest, *Photoresist Materials and Processes*, McGraw-Hill, New York (1975).