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.”

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 Senefelder 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.

2A. Senefelder, Vollständiges Lehrbuch der Steindruckerei [A Complete Course in Lithography, in German], Karl Thiemann, 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 \(p'q'/pq = klk'\).

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 mention 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

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158\(\text{ibid.},\ p. \text{327}.\)
160\(\text{ibid., p. 327}.\)
system, while the heat evolved is regarded as a measure of the diminution of the total energy of the system.\textsuperscript{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., $\frac{dp}{dT} = \frac{Q}{T}(v' - v)$, 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 $d \log p = \frac{Q}{RT}^2$, where $R$ is the universal gas constant.\textsuperscript{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.\textsuperscript{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: $\log K = -\frac{Q}{RT} + \text{constant}$. 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.\textsuperscript{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,

\begin{footnotesize}
\begin{enumerate}
  \item ibid., p. 329.
  \item ibid., p. 329.
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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

1 Lithography 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 (parrafined 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).
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.\textsuperscript{121} Memory devices lead the industry in both device density and linewidth.\textsuperscript{122} Packing density is determined by linewidth, so any increases in memory size require smaller linewidths or larger

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{growth_curves.png}
\caption{Growth curves for different IC devices that have been technology drivers over the years (plot generated in the manner of Masuoka\textsuperscript{120}).}
\end{figure}

\textsuperscript{122}ibid.
they are turning to multicore systems only because the path to higher clock speeds seems to be very difficult, at least for now.\textsuperscript{129}

The causes of this impasse derive from the peculiar physical and economic laws that govern the design of ICs.\textsuperscript{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,\textsuperscript{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.\textsuperscript{132}

Less famous than Moore’s law but equally influential are several “scaling laws,” first formulated in 1974 by Robert H. Dennard and co-workers 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

\textsuperscript{128}https://en.wikichip.org/wiki/amd/microarchitectures/zen%2B.
\textsuperscript{129}ibid.
\textsuperscript{130}ibid.
\textsuperscript{132}See Fig. 1.1 in Chapter 1.
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.\textsuperscript{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

\begin{align}
R &= k_1 \frac{\lambda}{NA}, \\
\text{DOF} &= k_2 \frac{\lambda}{(NA)^2},
\end{align}

where $\lambda$ 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

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

The oldest photolithographic technique is contact printing,\textsuperscript{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
