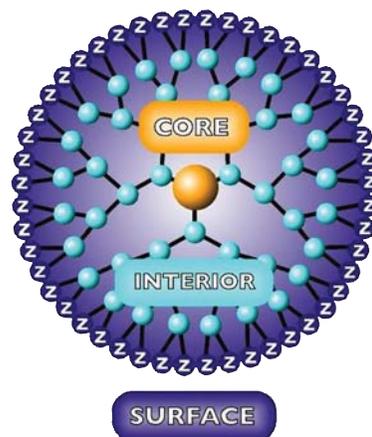
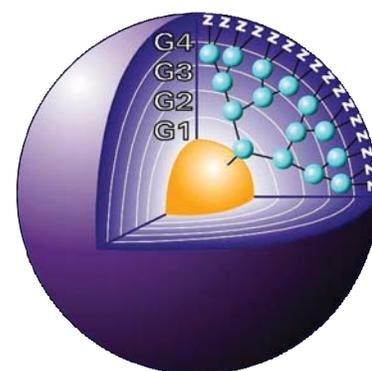
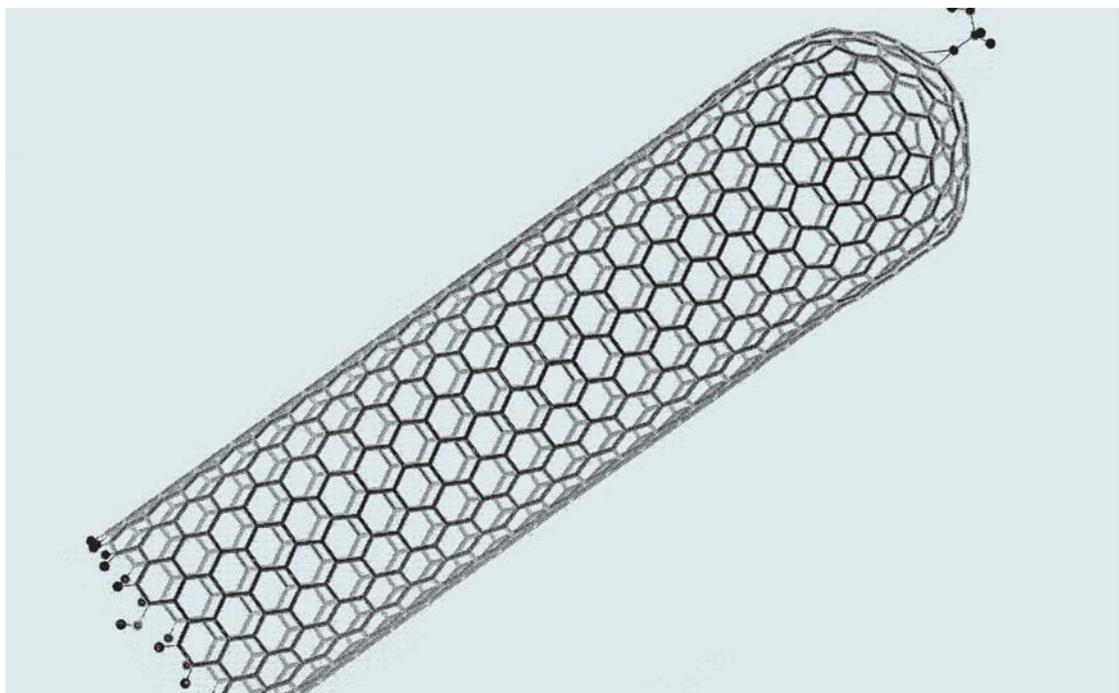


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# Studies in Materials Innovation

## Patterning the World: The Rise of Chemically Amplified Photoresists

David C. Brock

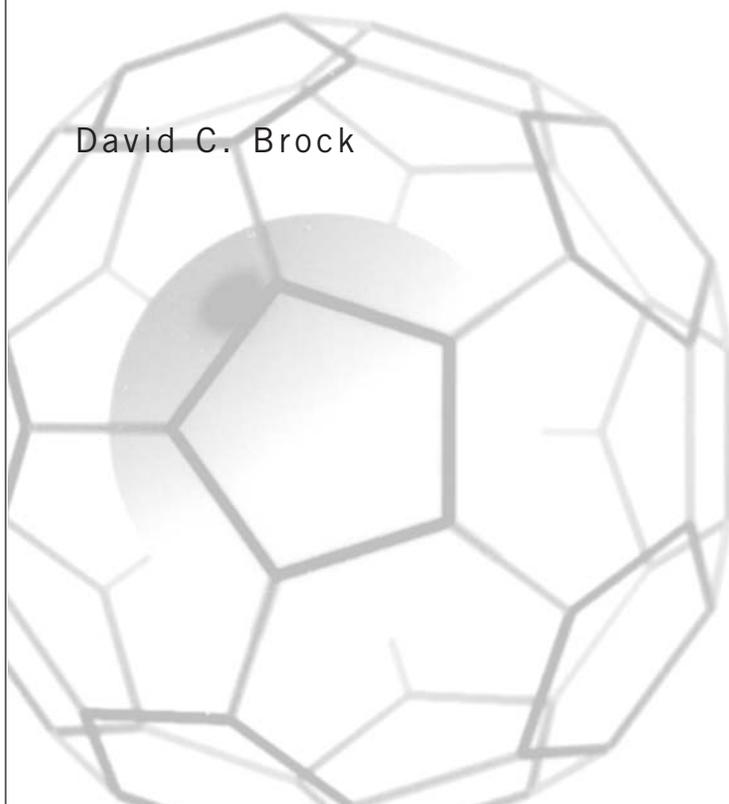


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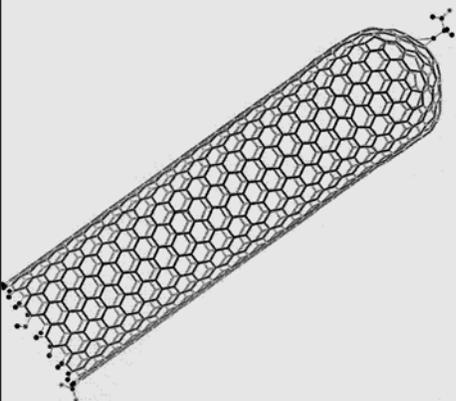
Studies in Materials Innovation

# Patterning the World: The Rise of Chemically Amplified Photoresists

David C. Brock



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# I. EXECUTIVE SUMMARY

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The rise of the Digital Age has been predicated on Moore's law—the observation, turned industrywide goal, that optimal economic advantage comes from an exponential increase in the performance of electronic components, accompanied by an exponential decrease in price. That is, the complexity of semiconductor devices should double every year or two, at a constant price. The realization of Moore's law over the last four decades has required unrelenting development of semiconductor manufacturing technology. Indeed, Moore's law is fundamentally about semiconductor manufacturing technology. This technology involves chemical and physical processes for depositing, chemically altering, and patterning thin films of materials on a silicon substrate. The rise of the Digital Age then is a story of continual materials innovation at a fundamental level.

In the early 1980s researchers in the semiconductor industry realized that the then dominant version of an absolutely central material on which semiconductor manufacturing technology was built—photoresist—would soon be insufficient, given the drive to maintain Moore's law. Therefore, a radically new form of photoresist would be required. This case study examines the innovation of the first of these radical “chemically amplified photoresists” by IBM in the 1980s.

The case supports four findings with implications for our understanding of the nature of innovation. First, the case shows the critical role of diverse individuals bringing aspects of their background experience to bear on a new area of inquiry, a constant process of partial transfer. These partial transfers were then hybridized with one another—in the sense of plant hybridization—resulting in the novel developments of the innovation process. Second, the case demonstrates the applicability of sociologist Andrew Pickering's notion of reciprocal structuring for understanding the process of materials innovation. Pickering describes a process by which researchers' intentions and materials are mutually reshaped through intensive interaction. This interplay gives rise to new knowledge, new intentions, and new materials with novel performance characteristics. Third, the case reveals the centrality of what I term imagined economies throughout the innovation process. Researchers' beliefs about economic factors profoundly shape their decision making, even preceding inventive activity. These economic beliefs of researchers, their imagined economies, are important factors throughout the entire innovation process. Fourth, the case shows the systemic nature of materials innovation: that is, orchestration as innovation. In semiconductor manufacturing an ecosystem of technologies exists. The innovation process for chemically amplified photoresists was motivated and bounded by an orchestration of elements in this technological ecosystem, most particularly lithography exposure tools.

## II. HISTORICAL NARRATIVE

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In the late twentieth century increasingly powerful and numerous personal computers, along with the networks interconnecting them, were at the center of shifts in work practices, communications, and cultural productions that collectively became known as the Digital Age. These personal computers were in no small part defined by two key types of electronic components: the microprocessor and the DRAM (dynamic random-access memory). These components in turn were species of silicon integrated circuits, owing both their existence and growing power to new developments in the manufacturing technology used to create them. Computer-chip manufacturers in the mid-1980s were pushing the limits of miniaturization using a variety of innovative manufacturing practices. The rise of the Digital Age depended on new materials and techniques that could both increase performance and drive down cost.<sup>1</sup>

For decades the semiconductor industry had used photolithography to build integrated circuits on wafers cut from large single crystals of the element silicon. In the patterning process of photolithography a polymer film called a photoresist is deposited over a thin film of one of a variety of materials deposited atop a silicon wafer. Next, in a complex (and expensive) apparatus known as an exposure tool, light of a very specific wavelength is projected through a pattern-bearing mask onto the photoresist. Regions of the photoresist exposed to the light undergo chemical changes, making them either more or less susceptible (depending on the process) to being removed in a subsequent chemical developing process. Thus the pattern of the mask is transferred to the photoresist. The pattern from the photoresist is then transferred to the underlying thin film through chemical etching. Multiple iterations of this thin-film patterning process, along with several other physical processes, produce integrated circuits. The photoresist is at the center of the photolithographic process, just as film used to be the crux of photography.<sup>2</sup>

In the late 1970s photolithographic procedures used light from the “near-ultraviolet (UV)” and “mid-UV” ranges at 365 and 313 nanometers (nm), respectively. Manufacturers realized that moving to a shorter wavelength, the so-called deep UV at 248 nm or less, would allow even smaller patterning of integrated circuits, thereby continuing the dynamics of miniaturization, exponential increases in functionality, and dramatic decreases in cost that characterize Moore’s law. Making the leap to deep UV would require significant materials innovations and a sea change in photoresist technology. An entirely new breed of photoresist—chemically amplified (CA) photoresists—created by

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<sup>1</sup>D. C. Brock, *Understanding Moore’s Law* (Philadelphia: Chemical Heritage Foundation, 2006).

<sup>2</sup>C. G. Willson, “Organic Resist Materials,” in *Introduction to Microlithography*, ed. L. F. Thompson, C. G. Willson, and M. J. Bowden, 139–267 (Washington, DC: American Chemical Society, 1994).

IBM in the early 1980s for just this purpose would eventually come to dominate global semiconductor manufacture. A more recent generation of CA photoresists tuned to 193-nm light has continued to enable Moore's law. For nearly two decades these photoresists have stood behind the Digital Age, largely unrecognized and undeservedly so.<sup>3</sup>

### PUSHING THE LIMITS AT IBM

Some commentators describe the digital computing business in the late 1970s as divided in halves, with IBM on one side and all other companies on the other. Despite thriving competitors in the minicomputer business and the appearance of the very first personal computers, IBM dominated the computer industry with its broad offering of mainframe and mid-range computer systems, largely produced by captive suppliers within IBM. Large semiconductor fabrication operations in East Fishkill, New York, and Burlington, Vermont, among other locations, produced integrated circuits as logic and memory components. Many materials for these semiconductor fabrication plants, or "fabs," came from additional operations in East Fishkill. In San Jose, California, a disk-drive manufacturing facility boasted a research laboratory. On the East Coast, Yorktown Heights, New York, was the site for the firm's research and development headquarters.<sup>4</sup>

Throughout the 1970s IBM produced its own photolithography equipment. As the decade drew to a close, however, IBM began to purchase significant numbers of sophisticated and expensive optical devices from the outside, particularly the Micralign lithography tools produced by the venerable optics house and chemical-instrumentation manufacturer Perkin Elmer. IBM's production facilities for advanced semiconductor components contained hosts of self—and Perkin Elmer—produced lithography "tools." These capital goods represented an enormous expenditure, with each tool having cost hundreds of thousands of dollars. In the same period the fate and future utility of these existing tools were being seriously questioned within IBM.<sup>5</sup>

By the time the 16K DRAM generation was launched in 1977, semiconductor memory was well on its way to displacing magnetic core memory as the dominant memory technology for digital computers. DRAMs were considered the shining examples of so-called "large-scale" and even "very-large-scale" integrated circuits in which huge numbers of components were squeezed onto tiny chips of silicon using the latest manufacturing technology, yielding expanded memory functionality at declining costs. Magnetic core memory, in contrast, hailed from the 1950s and consisted of great grid-like planes of wires with small metal rings at each intersection: think of the screen in a window, with a miniature washer around the corner of each little square. The magnetic states of these rings, or "cores," represented the digital language of 0s and 1s. First introduced in 1970, DRAMs were beating out cores in both performance and cost just six years later.<sup>6</sup>

<sup>3</sup> Brock, *Understanding Moore's Law* (cit. note 1); H. Ito, "Chemical Amplification Resists for Microlithography," *Advances in Polymer Science* 172 (2005), 37–245.

<sup>4</sup> See, for example, Martin Campbell-Kelly and William Aspray, *Computer: A History of the Information Machine*, 2nd ed. (Boulder, CO: Westview, 2004).

<sup>5</sup> William Brunsvold, interviews with David C. Brock, audio recordings and transcripts, 30 November 2006 and 7 December 2006; C. Grant Willson, interview with David C. Brock, audio recording and transcript, 20 December 2006; John Maltabes, interview with David C. Brock, audio recording and transcript, 27 November 2006.

The success of DRAM depended on the semiconductor industry's ability to push its manufacturing technology to its limits. Indeed, DRAM production became the bellwether for semiconductor manufacturing technology. The semiconductor industry, led by Intel, had established a metronomic pattern in which the industry launched a new generation of DRAM with four times the capacity of the previous generation—1K, 4K, 16K—every three years. Each generation required a new level of miniaturization, thereby creating a fundamental link between DRAM generations and manufacturing technology.<sup>7</sup>

In 1977 a looming question for the semiconductor industry was whether the existing lithography tools for the 16K DRAM generation could be used again for the upcoming 64K DRAM generation, or perhaps even for the 256K DRAM generation. The ability to form smaller features depended on the wavelength of light used in the tool: the smaller the wavelength, the smaller the possible features. The existing lithography tools used 365-nm light in the near-UV region to expose patterns onto silicon wafers coated with photoresist. Could the existing lithography tools and photoresists be modified to work with smaller wavelengths of light? The economic consequence of the answer was significant. Millions could be saved if the useful life of the manufacturing equipment could be extended.<sup>8</sup>

### PAUSING AT 313

Extending the life of IBM's lithography tools and photoresists was a major challenge that C. Grant Willson took up when he joined a research group focused on polymer science and technology at IBM's San Jose facility. Willson, a Bay Area native, had earned his Ph.D. in organic chemistry at the University of California, Berkeley, and had been working at the University of California, San Diego, doing research in biochemistry. Although it was generally recognized in the semiconductor community that significantly lower wavelengths would eventually be needed to get the required miniaturization, the San Jose polymers group was exploring the extension of near-UV lithography for upcoming DRAM generations. The IBM researchers saw an opportunity to extend the usefulness of their tools by moving to an "intermediate wavelength," a halfway point between the current near-UV and the future deep-UV.<sup>9</sup>

The attraction of this intermediate step was savings: they could postpone the refitting of factories with the new tools and resists they knew would eventually be required for the deep-UV regime. Moreover, this intermediate wavelength step—to 313 nm from 365 nm—would buy the researchers time to tackle the more radical developments necessary for the eventual migration to deep UV. Willson's first great success in photoresists was to create a modified version of the standard type of near-UV photoresist, known as "DNQ-Novolac resists," that was tuned to

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<sup>6</sup> Brock, *Understanding Moore's Law* (cit. note 1).

<sup>7</sup> Ibid.

<sup>8</sup> Willson, interview (cit. note 5); Brunsvold, interviews (cit. note 5).

<sup>9</sup> Willson, interview (cit. note 5).

work with 313-nm light and to be compatible with existing lithography equipment. Willson's proprietary resist was used for both 313-nm and traditional near-UV lithography and in a few short years suffused IBM semiconductor manufacturing. The resist gave IBM a competitive advantage in the form of tremendous cost savings by extending the utility of the company's existing tools and device performance advantages through successful miniaturization. Willson had established himself as a leader in photoresists within IBM.<sup>10</sup>

By 1979 Willson was focusing on a more challenging prospect: the move to deep UV. By this time IBM was anticipating the delivery of a new Perkin Elmer lithography tool to its fabs—the Perkin Elmer Micralign 500. This tool used a mercury lamp that generated UV radiation with intensity peaks at 365, 313, and 248 nm. The use of an appropriate filter made the tool capable of operating at any one of these wavelengths, and 248 nm was in the deep-UV region. At that wavelength the lamp emitted only one-thirtieth the amount of light as it did in the other UV regions. This relative dimness raised serious challenges.<sup>11</sup>

Existing photoresists did not have enough sensitivity to function with such a low intensity. A work-around was possible by using unprecedentedly long exposure times, but that was an economic nonstarter. Grindingly slow fabs would destroy any savings from extending the usable life of the tools. The IBM researchers had two remaining options: create a new lamp for the tools that was thirty times brighter at 248 nm, or invent a photoresist that was thirty times more sensitive to 248-nm light than the DNQ-Novolac resists.<sup>12</sup>

## A CHEMICAL SOLUTION

Willson increasingly focused on the chemical challenge: could he create a new photoresist with thirty times the sensitivity? He discussed this situation with Jean Fréchet, a visiting scientist who joined his group in the first days of 1979. Fréchet, born in France, was a polymer chemist on sabbatical at IBM's San Jose facility from the University of Ottawa. In discussions between the two chemists the essence of the needed innovation emerged: chain reactions. They imagined a photoresist in which a single photochemical event—the absorption of a photon by a material in the resist—could generate a cascading chain reaction. The chemistry of the photoresist would amplify the effect of the photochemical event, yielding the great sensitivity that was their goal.<sup>13</sup>

<sup>10</sup> Brunsvold, interviews (cit. note 5); Maltabes, interview (cit. note 5); Willson, interview (cit. note 5).

<sup>11</sup> Willson, "Organic Resist Materials" (cit. note 2); H. Ito, "Chemical Amplification Resists: History and Development within IBM," *IBM Journal of Research and Development* 41 (1997), 69–81; H. Ito, "Chemical Amplification Resists: Inception, Implementation in Device Manufacture, and New Developments," *Journal of Polymer Science: Part A: Polymer Chemistry* 41 (2003), 3,863–3,870; J. H. Bruning, "Optical Lithography—Thirty Years and Three Orders of Magnitude: The Evolution of Optical Lithography Tools," *Proceedings of the SPIE* 3049 (1997), 14–27.

<sup>12</sup> Willson, "Organic Resist Materials" (cit. note 2); Ito, "Resists: History and Development" (cit. note 11); Ito, "Resists: Inception, Implementation" (cit. note 11); K. Jain, C. G. Willson, and B. J. Lin, "Ultrafast High-Resolution Contact Lithography with Excimer Lasers," *IBM Journal of Research and Development* 26 (1982), 151–159; K. Jain, C. G. Willson, and B. J. Lin, "Ultrafast Deep UV Lithography with Excimer Lasers," *IEEE Electron Device Letters* EDL-3 (1982), 53–55; R. T. Kerth, K. Jain, and M. R. Latta, "Excimer Laser Projection Lithography on a Full-Field Scanning Projection System," *IEEE Electron Device Letters* EDL-7 (1986), 299–301.

Fréchet quickly advanced a particular polymer as a possible candidate for use in such a system: polyphthalaldehyde (PPHA). This polymer chain is unstable at room temperature; its propensity is to unzip, to depolymerize. Fréchet and Willson considered the possibility that irradiation could directly break bonds in the backbone of the polymer, causing the PPHA to depolymerize. Once the process began, the polymer would unzip itself in a chain reaction.<sup>14</sup>

Fréchet synthesized PPHA samples so that he and Willson could begin to work with the polymer. By the summer of 1979, however, it became clear to Fréchet that the project could not be completed before his sabbatical ended. Specifically, the photoresist project would require PPHA material with enhanced temperature stability. Getting temperature-stable PPHA, in turn, required that the material be produced using a specialized experimental procedure—*anionic polymerization*—involving a high-vacuum and complex glassblowing. At Fréchet's urging Willson made a recruiting trip to the chemistry department at the State University of New York's College of Environmental Science and Forestry in Syracuse, where Fréchet had earned his Ph.D. The university, Fréchet knew, was home to a research group famed for their prowess in *anionic polymerization*. There Willson met Hiroshi Ito, a research associate in the chemistry department who had a Ph.D. in polymer chemistry from the University of Tokyo and experience with the special techniques required for making PPHA. Willson offered Ito a postdoctoral position in his San Jose group, and in the summer of 1980 Ito joined the lab.<sup>15</sup>

Ito took over where Fréchet had left off, beginning by synthesizing PPHA using the new means in order to produce a more temperature-stable polymer. The new approach yielded PPHA with clean end caps of chemical groups at the ends of the backbone chains. These caps gave the new PPHA its improved temperature stability. Ito irradiated his PPHA, and the result was more a fizzle than a chain reaction. Depolymerization occurred, but it was woefully far from complete. Ito's next move was to incorporate a well-known photosensitive material into PPHA and to expose the resulting samples to deep-UV light. Half of the PPHA unzipped. This result was far better but still not good enough.<sup>16</sup>

Ito alighted next on the idea of using another, quite different kind of photoactive substance with his polymer: a photoacid generator (PAG). These compounds generate acid when they are exposed to light. Since both the PPHA backbone chain and its capping group could be cleaved by acid, Ito thought a PAG might initiate the desired chain reaction.<sup>17</sup>

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<sup>13</sup> Jain, Willson, and Lin, "Ultrafast High-Resolution Contact Lithography" (cit. note 12); Jain, Willson, and Lin, "Ultrafast Deep UV Lithography" (cit. note 12); Jean Fréchet, interview with Christophe Lécuyer, audio recording and transcript, 2 June 2006, Oral History Collection, Chemical Heritage Foundation, Philadelphia; Willson, interview (cit. note 5).

<sup>14</sup> Ito, "Chemical Amplification Resists for Microlithography" (cit. note 3); Willson, "Organic Resist Materials" (cit. note 2); Fréchet, interview (cit. note 13); Hiroshi Ito, interview with David C. Brock, audio recording and transcript, 11 December 2006; Willson, interview (cit. note 5).

<sup>15</sup> Ito, interview (cit. note 14); Fréchet, interview (cit. note 13); Willson, interview (cit. note 5).

<sup>16</sup> Ito, interview (cit. note 14); Ito, "Resists: Inception, Implementation" (cit. note 11).

<sup>17</sup> *Ibid.*

At this time a new class of PAGs based on onium-salt compounds had recently emerged from both 3M and General Electric. These generators produced notably strong acid, and many had the added virtue of being stable at high temperatures. The potential of these new PAGs for polymer chemistry was broad, and they quickly generated interest. Willson learned about the 3M PAGs at about the same time Ito alighted on the GE PAGs. Ito had been searching for another PAG to add to PPHA—one that was more temperature stable and produced stronger acid than the traditional PAGs. At General Electric the chemist James Crivello had invented triphenylsulfonium hexafluoroantimonate (TPSHFA) for UV-induced polymerization, or “curing,” of epoxy resins. This onium salt generated a strong acid that catalyzed the polymerization. Ito hoped Crivello’s onium-salt PAG would initiate a strong chain reaction of unzipping in Ito’s PPHA photoresist system.<sup>18</sup>

Willson vividly recalls the day when Ito first tested his novel mixture of PPHA and Crivello’s PAG as a deep-UV photoresist. The results, Willson recalls, were “remarkable.” With the new onium-salt PAG and a dose of UV light a *hundred* times less intense than that used in conventional photolithography, the PPHA rapidly and fully unzipped. Not only did the materials unzip, but also the exposed regions of Ito’s mixture completely vaporized, laying bare the underlying substrate. Ito’s material was a dramatic proof of concept of the chemical amplification scheme that Willson and Fréchet had advanced the previous year. At hand was a material with high resolution (the ability to produce fine patterns), high speed, and tremendously improved sensitivity to deep-UV radiation. Yet Ito’s PPHA system at once worked too well and not well at all. The vaporized photoresist material would hopelessly contaminate the lithography tools. Further, PPHA’s susceptibility to acid meant that it could offer little protection from acidic etching procedures and hence would be of little to no utility in actual device fabrication.<sup>19</sup>

Willson and Ito turned to another polymer that Fréchet had worked on during his sabbatical at IBM San Jose in 1979: poly(p-hydroxystyrene), or PHOST. PHOST is a styrene-based polymer, chemically similar to the Novolac resins used in conventional photoresists. Willson considered modifying PHOST to include a new side chain: tertiary-butoxycarbonyl, or tBOC. The resulting polymer was poly(p-t-butyloxycarbonyloxystyrene), or PBOCST. Willson, who had worked mainly in biochemistry before joining IBM, was aware that tBOC—a mainstay in peptide work—was susceptible to cleavage from the basic polymer through the action of both heat and acid. Ito also began investigations of photoacid-catalyzed cleavage of a different tBOC-protected polymer as a potential basis for a chemically amplified resist. Like Willson, Ito had gained experience with protective groups like tBOC before coming to IBM, synthesizing biochemically important polymers at SUNY.<sup>20</sup>

After looking at Ito’s results Willson and Ito decided to pursue a hybrid course: mixing PBOCST with the onium-salt PAG. The result of this mixture—this brew resulting from

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<sup>18</sup> Ito, interview (cit. note 14); Willson, interview (cit. note 5); J. V. Crivello, “The Discovery and Development of Onium Salt Cationic Photoinitiators,” *Journal of Polymer Science: Part A: Polymer Chemistry* 37 (1999), 4,241–4,254; G. H. Smith and J. A. Bonham, “Photosolubilizable Compositions and Elements,” U.S. Patent 3,779,778, filed 9 February 1972 and issued 18 December 1973 (3M was the assignee).

<sup>19</sup> Willson, interview (cit. note 5); Ito, interview (cit. note 14).

<sup>20</sup> Willson, interview (cit. note 5); Fréchet, interview (cit. note 13); Ito, interview (cit. note 14); Ito, “Chemical Amplification Resists for Microlithography” (cit. note 3); Willson, “Organic Resist Materials” (cit. note 2).

the experiences and interests of Fréchet, Willson, and Ito—stopped the researchers in their tracks. The tBOC resist displayed dramatic chemical amplification. After exposing the tBOC resist to 248-nm deep-UV light, the resist-coated silicon wafer was heated in a post-exposure bake. The acid generated by the onium salt catalyzed the cleavage of the tBOC groups. The resulting fragments then generated additional acid, catalyzing further tBOC cleavages in a cascade of deprotection. The reaction was both extremely fast and extraordinarily sensitive to the deep-UV light. At the beginning of his search for a CA resist Willson knew he needed a thirtyfold improvement in sensitivity over conventional resists. With the tBOC resist, Willson, Fréchet, and Ito had generated a hundredfold to two hundredfold improvement.<sup>21</sup>

By 1983 Willson was confident enough in the new tBOC resist to promote it within IBM. At the East Fishkill facility he presented the new resist to a collection of researchers and engineers from a variety of IBM sites, including representatives from East Fishkill's own photoresist operation and staff from the cutting-edge fab in Burlington, Vermont. John Maltabes, a lithography engineer from the Burlington plant, had been helping develop a manufacturing process for a 1Mb DRAM using deep-UV radiation to meet a "one micron design rule." Deep-UV lithography would be used to produce features as small as one micrometer (one millionth of a meter) on the new powerful memory chip. Maltabes had been evaluating the possibility of replacing the mercury lamps within the Perkin Elmer lithography tools in Burlington with excimer lasers. But Willson's tBOC presentation persuaded Maltabes that using the new photoresist with the existing mercury lamps was the better strategy: when he returned to Burlington, Maltabes tried to convince his supervisors to kill his project. Three months later they did just that. Maltabes's new job would be to help implement the tBOC resist for manufacturing the 1Mb DRAM.<sup>22</sup>

### SOMETHING IN THE AIR?

IBM had staked the future of its cutting-edge products on CA photoresists. The advantages were tremendous: the tBOC resist could save IBM millions of dollars in modification and replacement of its existing lithography tools. The downside was the uncertainty about whether the new resists could be made to work in an active manufacturing environment.

Production trials at Burlington, however, revealed new, unanticipated problems with the CA resist. For one, its sensitivity varied widely. After eliminating the lithography tools as the source of this unpredictability by installing new, exacting filters, the blame rested squarely on the tBOC resist. Eventually the production engineers in Vermont resorted to the kind of highly empirical "black magic" practices that characterized much of semiconductor manufacturing in its early years. They did not know why certain things worked, only that they did. The engineers found, for instance, that letting silicon wafers that had

<sup>21</sup> Ibid.

<sup>22</sup> Brunsvold, interviews (cit. note 5); Maltabes, interview (cit. note 5); Kerth, Jain, and Latta, "Excimer Laser Projection Lithography" (cit. note 12); S. J. Holmes, P. H. Mitchell, and M. C. Hakey, "Manufacturing with DUV Lithography," *IBM Journal of Research and Development* 41 (1997), 7–19; J. G. Maltabes et al., "1X Deep UV Lithography with Chemical Amplification for 1-Micron DRAM Production" *Proceedings of the SPIE* 1262 (1990), 2–7.

been coated with the tBOC resist sit for several hours in the factory before exposing them stabilized the sensitivity, but at a lower level.<sup>23</sup>

This variability in the sensitivity of the tBOC resist was truly troubling. Not only did it foreshadow unpredictability in the DRAM manufacturing; it also quite possibly meant problems with properly forming critical patterns on the DRAMs. The tBOC resist was needed to create the smallest features on the DRAMs. If the tBOC resist could not properly form these smallest features, the result would be fatally defective DRAMs.

The groups at San Jose, Burlington, and East Fishkill were troubled by the new resist's difficulties. Maltabes recalls a lunch conversation in San Jose about these issues in which an IBM researcher, Russ Wendt, who had experience manufacturing disk drives, suggested that these troubles stemmed from "something in the air." Wendt and his colleagues had attributed certain failures of disk drives to airborne contaminants and had used air-filtration systems with activated charcoal and HEPA filters to get around the problem. Surplus filtration units sat in a warehouse, and he offered them to the tBOC team.<sup>24</sup>

Maltabes and Scott McDonald from Willson's team returned to Burlington with the surplus units. With a series of experiments the pair determined that in filtered-air environments, and indeed environments of air pumped in from outside the fab, the resist sensitivity was both high and consistent. The atmosphere of the fab itself harbored contaminants that were responsible for the problems with the tBOC resist. With pressure mounting to get the 1Mb DRAM into full production, Burlington decided to filter the air rather than hunt down the unknown contaminant or contaminants. Once wafers were coated with the tBOC resist, they remained in a filtered-air environment until they entered the lithography tool.<sup>25</sup>

By 1986 1Mb DRAM production was in full swing. IBM manufactured several million of these DRAMs, all dependent on the CA tBOC resist. Reflecting the criticality of this resist to the success of this project in moving IBM to the first deep-UV manufacturing technology, the firm kept the resist as a proprietary material and the use of filtered air as a closely held trade secret into the early 1990s. Several million working DRAMs within IBM's flagship computer products offered powerful testimony: the era of CA photoresists had arrived.<sup>26</sup>

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<sup>23</sup> Brunsvold, interviews (cit. note 5); Maltabes, interview (cit. note 5); Holmes, Mitchell, and Hakey, "Manufacturing with DUV Lithography" (cit. note 22); Maltabes et al., "1X Deep UV Lithography" (cit. note 22); Ito, interview (cit. note 14); Ito, "Resists: Inception, Implementation" (cit. note 11).

<sup>24</sup> Maltabes, interview (cit. note 5); Maltabes et al., "1X Deep UV Lithography" (cit. note 22); Ito, interview (cit. note 14).

<sup>25</sup> Maltabes, interview (cit. note 5); Maltabes et al., "1X Deep UV Lithography" (cit. note 22); Ito, interview (cit. note 14); Willson, interview (cit. note 5).

<sup>26</sup> C. P. Ausschnitt, A. C. Thomas, T. J. Wiltshire, "Advanced DUV Photolithography in a Pilot Line Environment," *IBM Journal of Research and Development* 41 (1997), 21–37; Holmes, Mitchell, and Hakey, "Manufacturing with DUV Lithography" (cit. note 22); Ito, "Resists: History and Development" (cit. note 11); Maltabes et al., "1X Deep UV Lithography" (cit. note 22); J. M. Shaw et al., "Negative Photoresists for Optical Lithography," *IBM Journal of Research and Development* 41 (1997), 81–94.

## TRAJECTORY

For IBM, possession of the first CA photoresist conferred significant competitive advantage. By the mid-1990s, however, a combination of accidental and systematic factors broke IBM's exclusive hold on this class of material. Willson, Fréchet, and Ito had patented the tBOC resist in 1982, but the patent was limited to a particular group of CA resists defined by certain chemical characteristics and did not cover the very idea of a CA photoresist. This limited scope was the product of multiple factors: the large role played by the researchers rather than attorneys in writing the patent since others at IBM had deemed the work less than patentworthy; the vagaries of patenting chemical *processes* in comparison with patenting particular *materials*; and the existence of “prior art” in the patenting process. One of the developers of onium-salt photoacid generators at 3M, George Smith, had previously patented a photoresist involving a very similar mechanism to the tBOC resist. Thus, the limited scope of the IBM patent was required to keep from infringing on the territory defined by Smith's existing patent. These accidental factors allowed commercial photoresist producers—inspired by IBM's success—to bring their own versions of CA deep-UV resists to the market by the early 1990s.<sup>27</sup>

More systematically, CA photoresists escaped IBM as the computer giant participated in the growing trend among semiconductor manufacturers to obtain manufacturing equipment and materials from specialized external suppliers. As IBM came to rely more heavily on lithography tools produced by outsiders, the close coupling of tool with resist meant not only that the tool makers would need access to the best CA resists but also that the tool makers' other customers would require access. Moreover, specialized photoresist houses had greater resources and incentives for pushing CA photoresists forward. In the mid-1990s IBM actively transferred the second—and third—generation CA photoresists developed by Ito and others to the outside world. In this way IBM accelerated future developments in CA resists, empowering the continued evolution of the Digital Age.<sup>28</sup>

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<sup>27</sup> H. Ito, C. G. Willson, and J. M. J. Fréchet, “Positive- and Negative-Working Resist Compositions with Acid Generating Photoinitiator and Polymer with Acid Labile Groups Pendant from Polymer Backbone,” U.S. Patent 4,491,628, filed 23 August 1982 and issued 1 January 1985 (IBM was the assignee); Ito, interview (cit. note 14); Willson, interview (cit. note 5); Ito, “Resists: Inception, Implementation” (cit. note 11); Smith and Bonham, “Photosolubilizable Compositions and Elements” (cit. note 18).

<sup>28</sup> Brock, *Understanding Moore's Law* (cit. note 1); Brunsvold, interviews (cit. note 5); Michael McCoy, “Irresistible Force: Photoresist Makers Look Past 2001 Downturn to Next-Generation Products for Growth,” *Chemical & Engineering News* 80(2002), 23–24; J. S. Petersen and J. D. Byers, “Resist Requirements in the Era of Resolution Enhancement Techniques,” *Proceedings of the SPIE* 5039 (2003), 15–21; E. Reichmanis and L. F. Thompson, “Polymer Materials for Microlithography,” *Chemical Reviews* 89 (1989), 1,273–1,289; Shaw et al., “Negative Photoresists for Optical Lithography” (cit. note 26).

# III. FINDINGS

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## 1. PARTIAL TRANSFER AND HYBRIDIZATION

The early history of chemically amplified photoresists centers on a recurring pattern of diverse individuals bringing aspects of their varying backgrounds to bear on a new area of inquiry—a repeated process of *partial transfers*. These partial transfers of knowledge, materials, tools, techniques, skills, and approaches were *hybridized* with one another—in the sense of plant hybridization—resulting in the novel developments of the innovation process. Two specific instances of the dynamic involving the hybridization of the elements of partial transfers are particularly dramatic.

The first instance is that of the initial tBOC photoresist chemistry itself. Ito, Willson, and Fréchet all brought selected elements of their individual backgrounds and expertise to bear in the effort to create a chemically amplified photoresist. The partial quality of these transfers was critical. Willson, for example, through his earlier work in biochemistry was familiar with tBOC chemistry. By using just this aspect of his biochemical background for the photoresist effort, stripped of other biochemical approaches and procedures, Willson's tBOC transfer was open ended. It was amenable to hybridization with the contributions of others, like Ito's transfer of onium-salt photoacid generators. Similarly, Ito's importation of the 3M onium-salt photoacid generator was a partial transfer. Stripped was any vestige of the earlier use of the materials at 3M for the industrial curing of epoxies.

A similar process of partial transfer and creative hybridization is evidenced in the establishment of air filtering as part of IBM's semiconductor manufacturing technology in response to tBOC photoresist's susceptibility to airborne contamination. Partial transfers of knowledge and equipment from disk-drive manufacturing were brought into the arena of semiconductor manufacturing technology through discussion and exchange between individuals from diverse backgrounds. The partial transfer of air-filtration practices in disk-drive manufacture allowed for hybridization with lithography exposure tools to create novel practices supporting the use of CA photoresist.

Viewing this dynamic of partial transfer and hybridization as a centerpiece of the innovation process has direct implications for the theoretical systems and actions of individuals tasked with innovation management over a range of scales. This case study suggests that innovation managers should promote processes wherein individuals with deep expertise in particular disciplines are encouraged to bring elements of their backgrounds to bear on a new problem area outside their traditional disciplinary scope. This finding is in keeping with others that encourage multidisciplinary action.

## 2. RECIPROCAL STRUCTURING

The case of CA photoresists demonstrates the applicability of sociologist Andrew Pickering's notion of *reciprocal structuring* for understanding the general framework in which innovations occur. Pickering describes a process by which researchers' intentions and material systems—for example, the array of material samples and instrumental tools in a laboratory—are mutually adjusted in a process of intensive interaction. This interplay gives rise to new knowledge, new intentions, and new materials and physical systems with novel performance characteristics. All the key developments in the innovation of CA photoresists occurred during periods of just such intense, sustained interplay.<sup>29</sup>

The reciprocal structuring of researchers' intentions with the development and performances of new materials can be seen clearly at several points in the path leading to IBM's first tBOC photoresist. Perhaps the first of these instances provides the most direct example. Fréchet and Willson's understanding of the chemistry of PPHA led them to target this material initially as a candidate for a CA deep-UV photoresist. Ito's work with a high-quality, photosensitized sample of PPHA revealed the great sensitivity of the material but also showed that the complete evaporation of the material when exposed to deep-UV radiation rendered it a process contaminant rather than a photoresist. Thus, through a deep engagement with the materials and their performances, the researchers' intentions adjusted: they were even more confident in the chemical-amplification concept, but they were also convinced that a suitable polymer would need to be found with a chemistry quite different from PPHA.

The applicability of Pickering's framework to the case of CA photoresists thus highlights the fundamental import of *materiality*. The existing innovation-studies literature is overwhelmingly knowledge centered. That is, innovation studies by and large begin with the premise that innovation and invention are primarily knowledge-based processes. Within this viewpoint the generation of new knowledge and the access to existing knowledge are the key determinants of the innovation process and, as such, are the foci of interventions with the intent of fostering innovation. The case of CA photoresists as an exemplar of both recent materials innovation and Pickering's framework indicates that there is an important unexamined dimension to the innovation process, namely, the dimension of materiality. The production, distribution, modification, and networks associated with materials are—alongside knowledge—critical determinants of the innovation process. For the innovation manager this finding suggests the advisability of devoting attention to the role of materials in whatever innovation area is of concern and to the potential resources and constraints associated with materials.

## 3. IMAGINED ECONOMIES

This case study reveals the centrality of what I term “imagined economies” throughout the innovation process. In the literature of innovation studies the most common charac-

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<sup>29</sup> A. Pickering, “The Mangle of Practice: Agency and Emergence in the Sociology of Science,” *American Journal of Sociology* 99 (1993), 559–589; A. Pickering, *The Mangle of Practice* (Chicago: University of Chicago Press, 1995); A. Pickering, “Decentering Sociology: Synthetic Dyes and Social Theory,” *Perspectives on Science* 13 (2005), 352–405.

terizations of the innovation process hold that economic and market considerations are significant factors in the later stages of the innovation process—those stages closest to having a good or service available for consumption. In earlier stages, closer to “invention” than “innovation,” economic and market considerations are rarely discussed.<sup>30</sup> However, this case study demonstrates that researchers’ beliefs about economic factors profoundly shape their decision making, even preceding inventive activity.

Two examples from the case study draw out this point. First, at the earliest stage of development, that of *problem definition*, the very need for CA photoresists arose from frontline researchers’ beliefs about the economic contexts and consequences of their work. In particular, researchers’ views on the anticipated, or imagined, economics for the desirability of IBM avoiding large capital expenditures on new lithography tools as well as significant R&D costs on lithography-tool technology led the researchers to define a problem space for which their answer was the new concept of CA photoresists. In a profound way the quest for such a photoresist was an expression of the IBM researchers’ imagined economies. Second, and much later in the trajectory of the story, a critical factor that moved the first tBOC resist from being a research achievement at the San Jose laboratory to being a reality on the floor of the Burlington DRAM fab was the imagined economics of a then relatively junior lithography engineer. John Maltabes’s beliefs about the potential cost-benefit economics of the project to augment lithography tools with excimer lasers versus a project to incorporate CA resists into the existing ecosystem of fab tools and practices spurred the Burlington team to turn from lithography-tool innovation to CA photoresists for the important 1Mb DRAM production.

With these examples and many others this case study supports a finding at odds with, and corrective to, prevailing generalizations about the place of economics in the innovation process. Contrary to the dominant position in the innovation-studies literature that economic or market considerations are only significant in the final phases of innovation, the economic beliefs of researchers—their *imagined economies*—are important factors throughout the entire development of the innovation process. For the innovation manager this finding suggests the potential utility of expanded actions to provide frontline researchers with expert economic and market information about the firm, its current situation, and its forward-looking strategies and tactics.

#### 4. ORCHESTRATION AS INNOVATION

The history of the innovation of CA photoresists at IBM reveals a systemic feature of materials innovation. Within the innovation-studies literature, innovations are often said to be systemic in the sense of being produced by an “innovation system,” involving such macroscale elements as national research policy and government agencies. This case study evinces a quite different meaning of the systemic nature of materials innovation: that is, *orchestration as innovation*. In semiconductor manufacturing there exists an ecosystem of technologies. Within this ecology, lithography exposure tools and photoresists are highly coupled: the performances and characteristics of each help define the

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<sup>30</sup> For the current state of the art in the innovation studies literature, see the excellent and comprehensive J. Fagerberg, D. C. Mowery, R. R. Nelson, eds., *The Oxford Handbook of Innovation* (Oxford: Oxford University Press, 2005).

fitness and success of the other. Thus, the innovation process for CA photoresists was motivated and defined by an orchestration of elements of the technological ecosystem, most particularly lithography exposure tools.

Perhaps the clearest examples of the ecological and orchestrational character of materials innovation in the case of CA photoresist can be seen first in the early laboratory definition of the new material and second in the adaptations of the lithography tools in the fab required to create a hospitable environment for the new tBOC resist. In the first instance the relatively low-level output of the mercury vapor lamps of the Perkin Elmer Micralign lithography tools at the 248-nm wavelength was a key factor for defining the need for a new photoresist material. This element of the technological ecosystem created the need and set the conditions of fitness for the new CA photoresist. In the second instance the augmentation of the Perkin Elmer Micralign lithography tools in the Burlington fab with specialized air-handling systems and containers, in order to stabilize the performance of the tBOC photoresist, demonstrates adaptive, or orchestrational, pressure in the reverse direction. In this second instance the environmental demands of the tBOC resist for reliable performance necessitated the adaptation of the lithography tools.

It is this bidirectionality of the adaptive pressures that indicate the presence and importance of a technological ecosystem in this case study of materials innovation. For the innovation manager this finding suggests the desirability of increased attention to technological ecosystems as a defining context for innovations. Such increased awareness and attention could result in the identification of new lines of research, as well as enhanced understandings of potential pitfalls in and implications of existing lines of inquiry.

# IV. APPENDIXES

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## 1. METHOD

This case study was constructed from three classes of information sources. First, the author conducted substantial interviews with four individuals closely involved in the innovation of chemically amplified photoresists at IBM: Hiroshi Ito, C. Grant Willson, John Maltabes, and William Brunsvold. These interviews were audio-recorded and transcribed. Second, information was drawn from the published recollections of the three key innovators of the chemical amplification concept and the first chemically amplified resist materials: Hiroshi Ito, C. Grant Willson, and Jean Fréchet. Third, a wide array of technical publications and patents in this field were consulted.

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