

Planning Report 08-1

Economic Analysis of NIST's Investments in Superfilling Research

**Prepared by:
RTI International
for**

**National Institute of
Standards & Technology**

September 2008

NIST

**National Institute of
Standards and Technology**
U.S. Department of Commerce

September 2008

Economic Analysis of NIST's Investments in Superfilling Research

Final Report

Prepared for

Gregory C. Tasse
National Institute of Standards and Technology
100 Bureau Drive, Stop 1060
Gaithersburg, MD 20899-1060

Prepared by

Brent R. Rowe
Albert N. Link
Dorota S. Temple
Alex V. Rogozhin
RTI International
3040 Cornwallis Road
Research Triangle Park, NC 27709

RTI Project Number 0209878.000

RTI Project Number
0209878.000

Economic Analysis of NIST's Investments in Superfilling Research

Final Report

September 2008

Prepared for

Gregory C. Tasse
National Institute for Standards and Technology
100 Bureau Drive, Stop 1060
Gaithersburg, MD 20899-1060

Prepared by

Brent R. Rowe
Albert N. Link
Dorota S. Temple
Alex V. Rogozhin
RTI International
3040 Cornwallis Road
Research Triangle Park, NC 27709

Contents

Chapter	Page
Executive Summary	ES-1
1 Introduction	1-1
1.1 Need for NIST’s Involvement	1-2
1.2 Project Scope and Goals	1-3
1.2.1 Limitations	1-3
1.2.2 Key Study Objectives	1-4
1.3 Report Organization	1-4
2 Superfilling: Technical Background and NIST Contributions	2-1
3 Quantitative Analysis	3-1
3.1 Establishing the Period of Analysis	3-1
3.2 Identifying Affected Stakeholders	3-2
3.3 The Counterfactual Evaluation Method.....	3-4
3.4 Research Costs and Quantified Private-Sector Benefits	3-6
3.5 Additional Nonmonetary Benefit Metrics	3-8
4 Measures of Economic Return	4-1
4.1 Evaluation Metrics Description.....	4-1
4.2 Evaluation Analysis and Results: Base Case and Extrapolated Cases	4-3
5 Conclusions	5-1
5.1 Additional Benefits	5-2
5.1.1 Preproduction and Production Cost Savings	5-2
5.1.2 Information Exchange and Objectivity	5-3
5.1.3 Accelerating Innovation and Future Benefits	5-4
5.2 Observations for NIST.....	5-4
6 References	6-1

Appendices

A	Additional NIST Superfilling Research Contributions	A-1
B	NIST Superfilling Presentations/Teaching	B-1
C	NIST Superfilling Publications.....	C-1
D	Interview Guide	D-1
E	Patents Citing NIST Superfilling Publications	E-1

Figures

Number	Page
2-1 Chip Architecture Introduced by IBM	2-2
2-2 Types of Profile Evolution in Damascene Plating	2-4
3-1 Primary and Secondary Knowledge Flows of NIST Superfilling Research	3-5

Tables

Number		Page
3-1	Major Stakeholders' Total Sales and Employment Data, by Company	3-3
3-2	Market Coverage of Relevant Stakeholders through Interviews	3-4
3-3	NIST Research Costs Relating to Superfilling (\$nominal and \$2008)	3-7
3-4	Private-Sector R&D Cost-Savings Benefits: Base Case (\$2008)	3-8
3-5	Nonauthor Citations to the Seven Hallmark Papers, by Year	3-9
4-1	NIST Research Costs and Private-Sector R&D Benefits: Base Case (\$2008)	4-3
4-2	Evaluation Metrics: Base Case	4-3
4-3	NIST Research Costs and Private-Sector R&D Benefits: Base Case and Extrapolated Cases (\$2008)	4-5
4-4	Evaluation Metrics: Base Case and Extrapolated Cases	4-5
4-5	R&D Benefits Estimates by Stakeholder Group (\$2008)	4-5

Executive Summary

The semiconductor industry has long recognized that critical dimensions of integrated circuits (ICs) would need to be continually reduced so that devices could become smaller, faster, and more power efficient. In the 1990s, the semiconductor industry supply chain was producing devices with critical dimensions of between 0.35 and 0.25 microns, using aluminum or an aluminum copper alloy to interconnect device components (e.g., transistors). For devices with critical dimensions of 0.20 microns or smaller, the electrical properties of aluminum were deemed no longer sufficient to support efficient device operation. Thus, the industry's roadmap determined that copper—a superior conducting material—would be needed to help manufacture smaller and faster semiconductor devices.

Certain technical barriers prevented a seamless transition from aluminum to copper, however, and substantial resources were needed for research aimed at solving copper-integration issues. The National Institute of Standards and Technology (NIST) allocated resources to assist the semiconductor industry during this period.

To implement this effort, a team of NIST researchers developed a new model for copper electroplating and developed new software codes for the industry to conduct modeling and simulations exercises. Because of its enhanced predictive capability, the Curvature Enhanced Accelerator Coverage (CEAC) model helped lower the cost of research and development (R&D) in copper electroplating and reduce the time from R&D to production (referred to by those in the industry as the preproduction time period). NIST has continued to support the

semiconductor industry through refinements of the model and further development of the electroplating process.

ES.1 PROJECT SCOPE AND GOALS

The NIST Program Office sponsored this economic evaluation study as a retrospective investment analysis to support its strategic planning activities. NIST is interested in estimating the impact that advances in measurement infratechnologies, generic technologies, and associated standards have had on the semiconductor industry and how new programs might be developed in the future. This study focused specifically on evaluating the impact of NIST's superfilling research on the R&D and production environments of the industry supply chain.

This analysis is also important for the semiconductor industry as part of its overall strategic planning processes. Analyzing past impacts and future needs can help companies and trade associations focus attention and investment dollars on technology development and measurement issues projected to show substantial returns from industry investment.

ES.1.1 Key Study Objectives

This study assessed the net benefits of NIST's superfilling research conducted between 1999 and 2002. To this end, it focused on the industry's use of NIST's research findings, including its analysis of the relationship between electrolytes and certain process characteristics of superfilling, and the industry's adoption of the CEAC model. Specifically, the main objectives of this study were to

- describe the historical discovery and development of the superconformal deposition (superfilling) process and NIST's role,
- estimate the industry's "adoption" and use of key research findings that NIST published between 2000 and 2003, and
- quantify the benefits of NIST's superfilling research work in terms of R&D cost savings and qualitatively evaluate the impact on process and product quality.

ES.2 SUPERFILLING: TECHNICAL BACKGROUND AND NIST CONTRIBUTIONS

In the late 1980s and early 1990s, the semiconductor industry determined that copper interconnects would eventually be needed to achieve higher chip performance at smaller sizes; however, many obstacles existed. After years of industry research, on September

22, 1997, IBM announced that it had developed a method for manufacturing semiconductor chips with copper circuits.

IBM's process depended on the use of electrolyte additives that affect the local deposition rate and result in bottom-up filling. However, IBM researchers did not fully understand the relationship between the additives in the electrolytes and the superfilling process characteristics. Specifically, they did not understand the "incubation period" of conformal deposition that preceded the bottom-up filling, the bottom-up filling itself, or the subsequent formation of bumps over superfilled features. In fact, IBM researchers were unable to predict even qualitatively the occurrence of such events for their existing superfilling electrolyte or any others that might be derived thereof.

NIST developed a model, called the CEAC model, which provided a means for predicting quantitatively the ability of alternate chemical additives to induce optimal superfilling. Chemical and material suppliers, equipment suppliers, and device manufacturers all benefited from a reduction in R&D costs associated with developing the next generation of ICs. Better predictive models reduced the need for trial and error processes and increased production yield rates.

Full use of the NIST model allowed identification of the optimal experimental parameters for void and seam-free feature filling with minimal overfilling principally through rapid, inexpensive studies on planar substrates and CEAC modeling rather than exhaustive, costly feature-filling studies. NIST's work enabled the following:

- more rapid screening of electrolyte systems for interconnect fabrication applications that accelerated implementation;
- quantitative prediction of electrolytes' efficacy that substantially reduced the time and effort involved in experimental fill studies for implementation in applications;
- improved processing through predictive understanding of the superfilling mechanism, including incubation period, bottom-up filling, and overfill bump formation; and
- extrapolation of existing results to more advanced (e.g., smaller) dimensions even prior to the availability of industrial patterned wafers with such filling geometries.

ES.3 QUANTITATIVE ANALYSIS

RTI International estimated the net economic benefits (private and social) accruing from NIST's research investment in superfilling characteristics and modeling. RTI focused specifically on the initial

development of NIST's CEAC model, the major aspects of which were first disseminated to the research community through seven published papers. These hallmark papers, written based on research conducted between 1999 and 2002, included several key accomplishments:

- linked hysteresis and bottom-up filling of trenches during copper deposition,
- described the equations that make up the CEAC model,
- demonstrated how the CEAC equations could be used to drastically increase the evaluation efficiency of key processing parameters (e.g., the incubation period, the shape and process of bottom-up filling, and overfill bump formation), and
- discussed how the expanded model could be used to predict the effects of changes in geometry.

The focus of the analysis was on the adoption and use of research knowledge and techniques as reflected through the seven hallmark papers referenced above. Costs were estimated for research, conducted between 1999 and 2002, that resulted in these papers.

Benefits for each potential application of NIST's research findings—in R&D, in the adoption of superfilling, and in production—were considered, but R&D cost savings were the only benefit that could be quantified. Interviews suggested that such benefits accrued to stakeholders between 2003 and 2005.

ES.3.1 Identifying Affected Stakeholders

NIST's research affected the industry by significantly improving the superfilling process and reducing R&D costs. More specifically, the following industry groups were affected:

- chemical and material suppliers,
- equipment suppliers,
- analytical tool suppliers, and
- device manufacturers.

Figure ES-1 conceptualizes the knowledge flows associated with NIST's research on superfilling. The figure illustrates the primary (bolder lines of impact) and secondary impacts of NIST's research as disseminated through the seven hallmark papers discussed above.

Figure ES-1. Primary and Secondary Knowledge Flows of NIST Superfilling Research

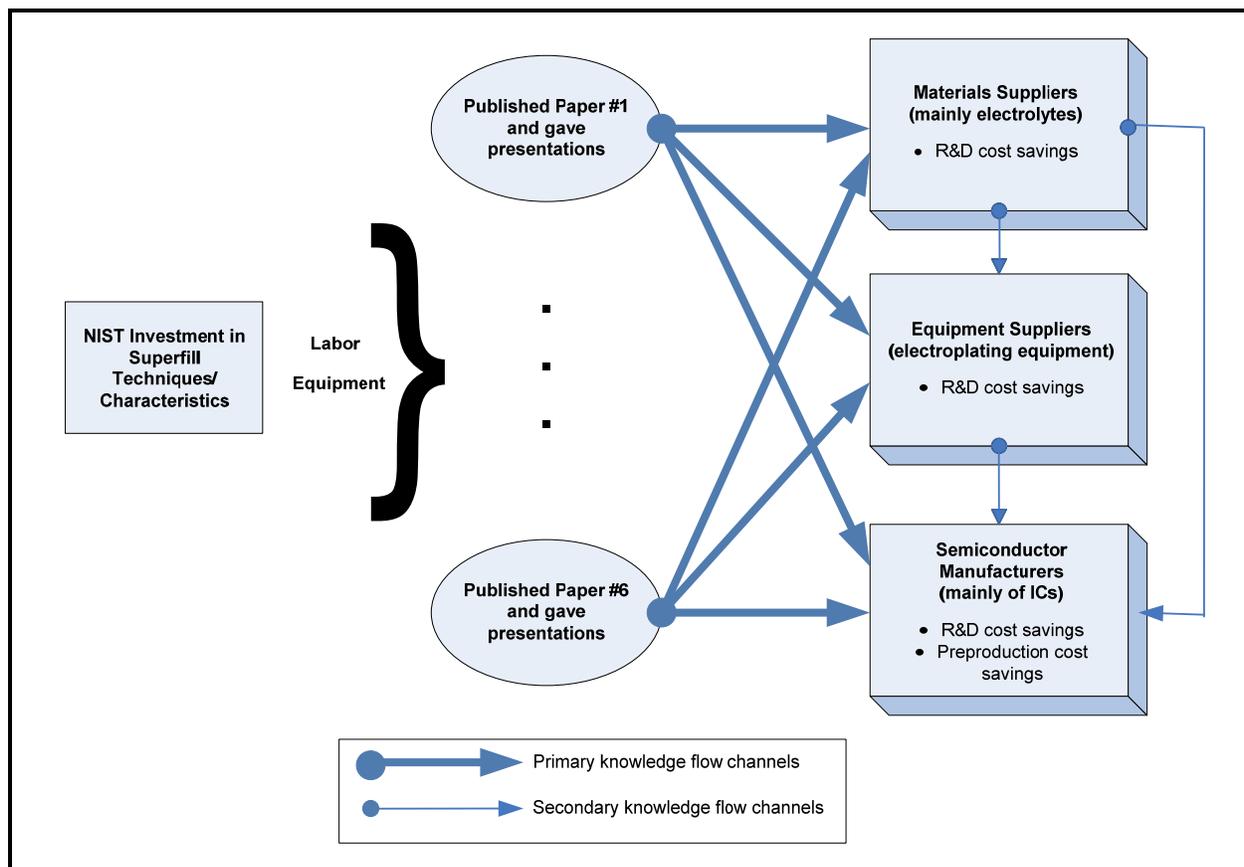


Table ES-1 provides approximate estimates of the market coverage represented by information collected during interviews. The “market” was estimated during interviews as the portion of companies’ sales relevant to superfilling chemicals, equipment, or tools (for chemical and material suppliers, equipment suppliers, and analytical tools suppliers) and the portion of device manufacturer products that used copper for interconnects and, hence, use a superfilling process during manufacturing.

ES.3.2 The Counterfactual Evaluation Method

RTI sought to determine whether the publicly funded research provided a unique capability or a result otherwise not possible or likely to occur (i.e., because private entities would not have been able to see a sufficiently positive private return on investment).

Table ES-1. Market Coverage of Relevant Stakeholders through Interviews

Stakeholder Group	Number of Firms	Approximated Market Share Represented by Sample Firms
Chemical and Material Suppliers	2	85%
Equipment Suppliers	2	80%
Analytical Tool Suppliers	3	50%
Device Manufacturers	4	80%

According to industry and expert interviews, NIST's research significantly altered the knowledge base and predictive capabilities of R&D within the industry related to the superfilling process. Although a handful of organizations were conducting research on superfilling characteristics and electrolyte properties when NIST first became directly involved in this research in 1999, prior to NIST's research and publications, the industry's R&D infrastructure was operating under several inaccurate assumptions regarding the superfilling process. As a result, the industry could not predict how to achieve optimal superfilling results. Progress by scientists outside NIST varied, but, according to industry stakeholders interviewed by RTI, all lagged significantly with regard to improving the predictive knowledge of the superfilling process relative to NIST's contributions.

Additional quantitative analysis related to the benefits of using NIST's research findings on, for example, preproduction and production activities was not possible. Relevant information was not documented by industry in "real time" when NIST research and results were being used; thus, industry members could not estimate the complex nature of the benefits.

ES.4 ECONOMIC COSTS AND BENEFITS

NIST incurred costs between 1999 and 2002 to undertake the research that culminated in the CEAC model described in their seven hallmark papers. These costs, in real 2008 dollars, are reported in column 1 of Table ES-2. The values in Table ES-2 include fully burdened labor (salary plus benefits), chemicals and materials, and equipment costs and overhead.

Table ES-2. NIST Research Costs and Private-Sector R&D Benefits: Base Case and Fully Extrapolated Case (\$2008)

Year	Real Cost	Real Cost-Savings Benefits	Real Cost-Savings Benefits: Fully Extrapolated
1999	\$287,500	\$0	\$0
2000	\$414,634	\$0	\$0
2001	\$394,048	\$0	\$0
2002	\$381,176	\$0	\$0
2003	\$0	\$1,920,000	\$3,643,333
2004	\$0	\$1,920,000	\$3,643,333
2005	\$0	\$1,110,000	\$1,762,500
2006	\$0	\$0	\$0
2007	\$0	\$0	\$0
Total	\$1,477,358	\$4,950,000	\$10,726,471
Net Present Value	\$1,330,339	\$3,573,332	\$7,759,035

The R&D and preproduction cost savings resulting from NIST's involvement most clearly could be defined as additional R&D costs that companies would have incurred absent NIST's research and the resulting model. Benefit estimates reflect the time period needed to replicate NIST's research results. On average, representatives reported that, beginning in 2003, a 2- to 3-year lag would have occurred before another organization would have developed the CEAC model.

Table ES-2 presents a total "base case" benefit estimate of almost \$5,000,000, which includes only benefits that RTI quantified directly through interviews. Estimates of the benefits of NIST's research were also extrapolated to the entire industry. Fully extrapolated benefits, also presented in Table ES-2, provide more probable metrics by which to gauge the cost-savings impact of NIST's investments.

Additional evaluation metrics are presented in Table ES-3. The full extrapolation resulted in a benefit-to-cost ratio was 5.83 and an internal rate of return 79.4%. Calculated net benefits for the industry were \$9,249,112 and a net present value (NPV) of \$6,428,697.

Table ES-3. Evaluation Metrics: Base Case and Fully Extrapolated Case

Metric	Value Based on Interview Data	Value Based on Full Extrapolation of Benefits
Costs (\$2008)	\$1,477,358	\$1,477,358
Benefits (\$2008)	\$4,950,000	\$10,726,471
Net Benefits (\$2008)	\$3,472,642	\$9,249,112
Benefit-to-Cost Ratio	2.69	5.83
Net Present Value (\$2008)	\$2,242,994	\$6,428,697
Internal Rate of Return	43.4%	79.4%

ES.5 CONCLUDING REMARKS

Quantified benefits estimates presented in this report may be considered conservative for several reasons and thus may understate the social benefits associated with NIST's research in superfilling. RTI's research suggests that the benefits from NIST's research go well beyond those quantified in this report. However, both the time that has elapsed since NIST's research was published and the difficulty involved in attributing benefits beyond R&D cost savings to new R&D research methods made accurately quantifying additional benefits very difficult.

Specifically, as successful R&D finds its way into production, production cost savings result. Device manufacturers, however, were unable to quantify impacts such as decreasing preproduction costs or accelerating the transition to production. NIST's work accelerated the preproduction process for the second generation of ICs that used copper for interconnects. Thus, manufacturers were able to develop higher-quality chips faster, resulting in reduced overall production costs and accelerating the market availability of the second-generation of ICs that used copper.

The knowledge embodied in the CEAC model and in the seven hallmark papers influenced other scientists, as evidenced by the paper-citation information in Table 3-5 and by the patent citation information in Appendix E. This diffusion of knowledge certainly endowed benefits to society, but these qualitative benefits were not considered in the analysis described in this report.

Further, NIST and industry have continued to build on the CEAC model since the publications that are the focus of this study. Over the last 5

years, NIST researchers have expanded the usefulness of the model through, for example, innovative research into the use of gold or silver for superfilling. Interview participants suggested that the CEAC model is still very useful to the industry and likely will be for the foreseeable future.

1

Introduction

This report documents the net economic benefits (private and social) accruing from the National Institute of Standards and Technology's (NIST's) research investments in superfilling during the late 1990s and early 2000s.

Since its early days, the semiconductor industry had recognized that critical dimensions of integrated circuits (ICs) would need to be continually reduced so that devices could become smaller, faster, and more power efficient. In the 1990s, the semiconductor industry supply chain—broadly defined to include chemical and material suppliers, equipment suppliers, analytical tool suppliers, and device manufacturers—was producing devices with critical dimensions of between 0.35 and 0.25 microns,¹ using aluminum or an aluminum copper alloy to interconnect device components (e.g., transistors). For devices with critical dimensions of 0.20 microns or smaller, the electrical properties of aluminum were deemed no longer sufficient to support efficient device operation. Thus, the industry determined that copper—a superior conducting material—would be needed to help manufacture smaller and faster semiconductor devices.

Certain technical barriers prevented a seamless transition from aluminum to copper, however, and substantial resources would be needed for research aimed at solving copper-integration issues. NIST's research aimed to assist the semiconductor industry during this period. The 1997 National Technology Roadmap for Semiconductors and the 1998 International Technology Roadmap for Semiconductors identified the technical limitations of aluminum and called for expanded research on the use of copper, which semiconductor experts believed could

¹ 1 micron is 1 millionth of a meter, or 10^{-6} meters.

significantly improve interconnect performance in highly sophisticated ICs.

IBM had begun researching the use of copper for interconnects in the late 1980s and, by the mid-1990s, pioneered a process called “superfilling.” In this process, copper would be electrochemically deposited (electroplated) in both vias, holes that connect one layer of a semiconductor chip to another, and the trenches overlapping the vias, to form the metal that “interconnected” device components. Alternatively, copper would be electroplated in both vias and trenches in a single step (called “dual damascene”).

Extending superfilling to increasingly smaller and higher aspect-ratio vias and trenches required continuous refinement of the composition of electroplating chemicals (electrolytes). The key challenge of this development was to fully understand the relationships between chemical additives and the superfilling characteristics of the electrolytes. These additives, called accelerators and suppressors, are the key components controlling the characteristics of copper electroplating in vias and trenches. In 1998, IBM researchers published a paper proposing a mechanism for the superfilling process (Andricacos et al., 1998); however, the proposed model was limited in its ability to predict electroplating “profiles,” which define how filling occurs. As a result, research and development (R&D) in the area of copper superfilling was inefficient: scientists continued to conduct analysis by a “trial and error” approach.

1.1 NEED FOR NIST'S INVOLVEMENT

To assist the semiconductor industry, a team of NIST researchers in the Metallurgy Division of the Materials Science and Engineering Laboratory (MSEL) at NIST conducted research into superfilling techniques. NIST researchers (including Daniel Josell, Thomas Moffat, and Daniel Wheeler) focused NIST resources, in the form of labor, equipment, chemicals, and materials, on the development of electroplating techniques, model and parametric characterization of process results, and development of software codes for modeling and simulations. This effort leveraged 2 years of NIST experience in copper electroplating.

Within 1 year (by the year 2000), NIST had developed a new model for predicting the characteristics of copper superfilling, based on adsorption of additives from the electrolytes onto the surface of the copper

electrodeposits within the filling features. NIST's Curvature Enhanced Accelerator Coverage (CEAC) model allowed for the prediction of copper profiles in vias and trenches, based on straightforward tests conducted on planar test samples.² Because of its enhanced predictive capability, the CEAC model helped lower the cost of R&D in copper electroplating and reduced the time from R&D to production (referred to by those in the industry as the preproduction time period). NIST has continued to support the semiconductor industry through refinements of the model and further development of the electroplating process.³

1.2 PROJECT SCOPE AND GOALS

The NIST Program Office sponsored this economic evaluation study as a retrospective investment analysis to support its strategic planning activities. NIST is interested in estimating the impact that advances in measurement infratechnologies, generic technologies, and associated standards have had on the semiconductor industry and how new programs might be developed in the future. This study focused on NIST's research on superfilling techniques. Evaluating the impact of this investment, which can most easily be seen in the R&D and production environments of the industry supply chain, was the purpose of this study.

This analysis is also important for the semiconductor industry as part of its overall strategic planning processes. Analyzing past impacts and future needs can help companies and trade associations focus attention and investment dollars on technology development and measurement issues projected to show substantial returns from industry investment.

1.2.1 Limitations

This analysis was unable to estimate quantitatively the impact of NIST's work on the quality of semiconductor devices or any cost savings in the production environment because of the difficulty involved in attributing production process and product improvements to specific R&D investments. The semiconductor industry moves very quickly, and speculation on what would have occurred without a key technology or technique is uncertain at best. In general, stakeholders indicated that they would likely have achieved the same or very similar product quality within the same time period without NIST's involvement, though at a higher cost. Many suggested that the process quality may have been

² The CEAC model is a mathematical model, not a physical model or tool.

³ See Appendix A for more details on NIST's related work on superfilling.

lower without NIST's research, which would have resulted in a lower manufacturing yield (i.e., fewer products per dollar of investment for sale to customers). Because we could not quantify such benefits, the impacts we present can be viewed as conservative (lower-bound) estimates.

1.2.2 Key Study Objectives

This study assessed the net benefits of NIST's superfilling research conducted between 1999 and 2002. To this end, it focused on the industry's use of NIST's research findings, including its analysis of the relationship between electrolytes and certain process characteristics of superfilling, and the industry's adoption of the CEAC model. Specifically, the main objectives of this study were to

- describe the historical discovery and development of the superconformal deposition (superfilling) process and NIST's role,
- estimate the industry's "adoption" and use of key research findings that NIST published between 2000 and 2003, and
- quantify the benefits of NIST's superfilling research work in terms of R&D cost savings and qualitatively evaluate the impact on process and product quality.

1.3 REPORT ORGANIZATION

The remainder of this report is organized as follows:

- Chapter 2 discusses in detail, from a technical perspective, the superfilling process and the importance of the advancements embodied in the CEAC model.
- Chapter 3 describes the methodology that RTI employed to assess the net economic benefits (private and social) associated with NIST's investments in the CEAC model.
- Chapter 4 discusses the findings from the evaluation analysis and provides a discussion of qualitative benefits.
- Chapter 5 concludes this report with a summary of findings.

2

Superfilling: Technical Background and NIST Contributions

Moore's Law states that the processing capabilities of ICs double every 2 years (Moore, 1965). Toward that objective, ICs have become smaller, and both materials and processing activities have had to evolve to achieve industry goals. In the late 1980s and early 1990s, the semiconductor industry determined that copper interconnects would eventually be needed to achieve higher chip performance at smaller sizes; however, as discussed in Chapter 1, many obstacles existed.

After years of industry research, on September 22, 1997, IBM announced that it had developed a method for manufacturing semiconductor chips with copper circuits. IBM claimed at that time to have "solved a fundamental problem holding back the development of faster semiconductor chips ... [and it will soon begin to manufacture chips] that are smaller and up to 40 percent more powerful than the most advanced chips currently being produced commercially" (Zuckerman, 1997).

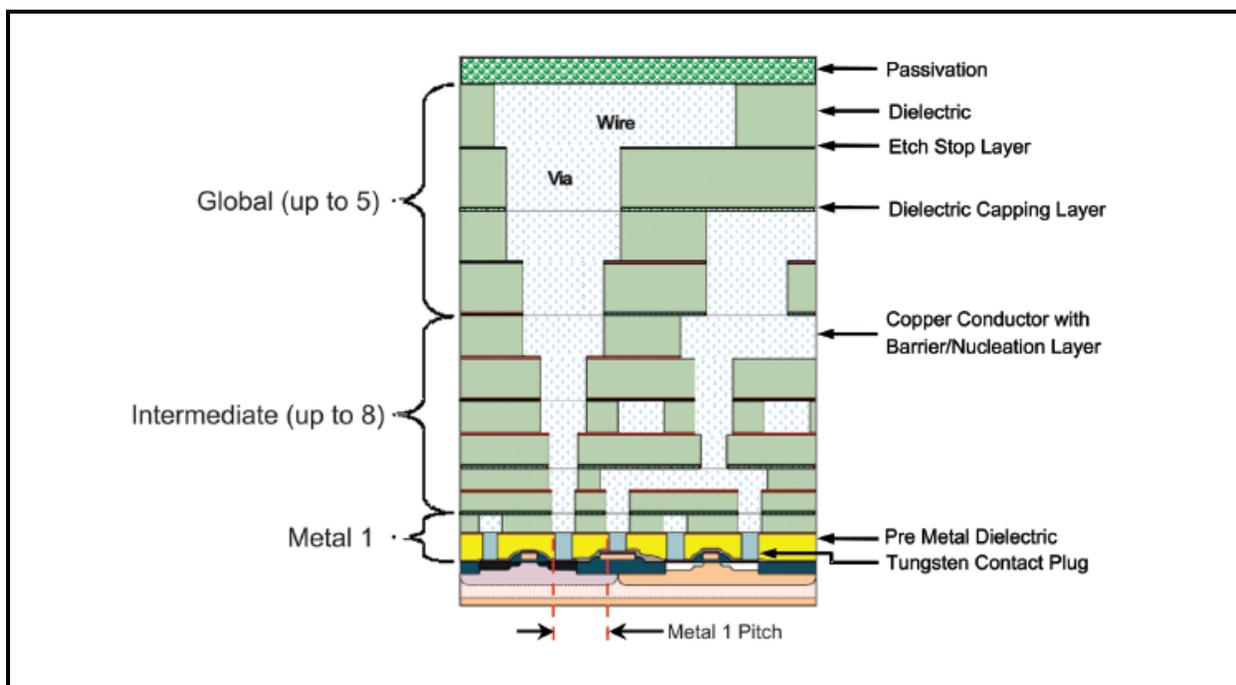
IBM's technological breakthrough was first described in the professional literature in 1998 by Andricacos (1998) and Andricacos et al. (1998). Andricacos (1998, p. 2) noted the following:

Use of copper as the interconnection conductor enables a decrease in the number of metal layers needed for the optimal operation of chips, especially if combined with an insulator that has a lower dielectric constant than silicon dioxide used presently. Because of its superior resistance to electromigration, copper wiring permits higher current densities without failure and therefore with higher reliability.

In enabling the copper electrodeposition process, IBM developed a new electroplating process, called “damascene” or dual “damascene electroplating,” in which the copper was deposited in trenches and vias prepatterned into the dielectric. This new fabrication method resulted in a new device architecture, which is illustrated schematically in Figure 2-1. Shown in Figure 2-1 is a cross-section of a portion of an IC, consisting of transistors (at the bottom of the sketch) and multilevel metal wiring structure above, which connects the transistors. In modern ICs, as many as 10 layers of wiring may be required to interconnect all the transistors in a circuit. The individual wiring layers are connected by holes (vias) filled with metal, as indicated in the schematic. The process of filling the vias is very challenging, especially as the vias get smaller in diameter and become deeper. In particular, previously used (“traditional”) electroplating techniques, in which the metal deposition proceeds at an equal rate at all points on the profiles of the via, resulted in the formation of voids. IBM’s new design and electroplating technique solved this problem.

Significantly, IBM demonstrated that during filling of these features “under certain conditions, electroplating inside trenches occurs

Figure 2-1. Chip Architecture Introduced by IBM



Source: Case (2004).

preferentially in the bottom leading to void free deposits. ... [and IBM called] this phenomenon superfilling” (Andricacos et al., 1998, p. 567).

IBM had been working on damascene electroplating for copper interconnects since 1989. Milestone accomplishments included the following (Andricacos et al., 1998):

- 1989: first demonstration of damascene copper electroplating for chip interconnects
- 1991: electroplating adopted for the development of a copper/polyimide bipolar device
- 1993: four-level copper polyimide paper published
- 1995: damascene electroplating passes feasibility tests
- 1997: first working microprocessor using copper damascene electroplating fabricated
- 1998: damascene electroplating in high-volume manufacturing¹

As shown in Figure 2-2, IBM’s superfilling process (or superconformal process), compared to a subconformal or conformal plating process, resulted in defect-free filling because the bottom surface of copper rises before the side walls close off. A side benefit of the process was that copper could be deposited into a combined layer of trenches and underlying vias simultaneously, and the associated reduction of separate deposition and polishing steps results in significant production-cost benefits.²

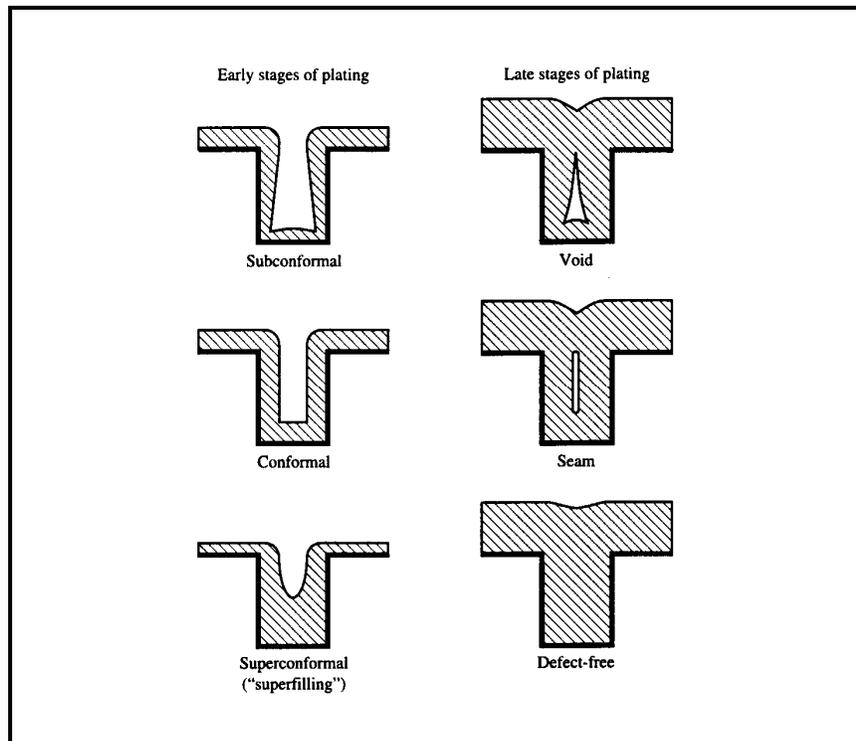
IBM’s process depended on the use of electrolyte additives that affect the local deposition rate and result in the bottom-up filling. However, IBM researchers did not fully understand the relationship between the additives in the electrolytes and the superfilling process characteristics. Specifically, they did not understand the “incubation period” of conformal deposition that preceded the bottom-up filling, the bottom-up filling itself, or the subsequent formation of bumps over superfilled features. In fact, IBM researchers were unable to predict even qualitatively the occurrence of such events for their existing superfilling electrolyte or any others that might be derived thereof.³

¹ AMD was an early adopter of IBM’s manufacturing process (Siegle, 2002).

² The need for polishing in semiconductor manufacturing resulted from the use of copper in the process. There was no polishing with aluminum; a lift-off process was used.

³ This conclusion is based on discussions with NIST scientists and the content of papers by Andricacos at IBM.

Figure 2-2. Types of Profile Evolution in Damascene Plating



Source: Andricacos et al. (1998).

In late 1999, Andricacos presented his research on copper superfilling in a seminar at NIST. The presentation, like IBM's written work on the topic, described a model that, even using nonphysical inputs, was unable to predict any of the unique characteristics of observed superfilling behavior noted above. Furthermore, questioning by Moffat, a NIST scientist in attendance who had been researching the deposition properties of copper plating electrolytes, revealed that IBM had not conducted surface or additive mass balance studies, such as might elucidate the mechanism by which void-free copper superfilling would occur.

To address these unresolved issues and to respond to obvious industry needs, NIST scientists expanded their laboratory research on electrolytes for copper deposition into feature superfilling, publishing several influential papers beginning in December 2000 (Moffat et al., 2000) and extending over the course of the following several years. In 2000, the NIST group demonstrated and fully disclosed the relationships between electrolyte chemical properties, the superfilling process, and deposit recrystallization.

As a result of their modeling work, NIST identified new individual additives and additive concentrations, the use of which would result in

much improved superfilling, as compared to so called first-generation commercial electrolyte chemistry used to produce the first generation of copper devices. Subsequently, the NIST approach became the prototypical or de facto system for the investigation and public discussion of superconformal feature-filling phenomena. The second-generation two-component suppressor-accelerator commercial chemistries in use today look very much like the NIST-identified electrolyte compositions.

In addition to identifying an electrolyte that generated the essential characteristics required for a successful superfilling process, NIST established a one-to-one linkage between transient deposition properties of electrolytes that manifest themselves as hysteresis⁴ during current-voltage cycling on planar (i.e., flat) surfaces and the ability of electrolytes to yield bottom-up filling of trenches during copper deposition (Moffat et al., 2000). The importance of this linkage was that it enabled rapid, inexpensive studies of deposition on planar surfaces to determine whether specific electrolytes would exhibit superfilling of trenches. The 2000 NIST paper also noted the linkage between hysteresis and the recrystallization of the copper deposited from such electrolytes; this recrystallization manifests itself as electrical resistivity that decreases at room temperature over the course of days, a beneficial phenomenon that IBM noted occurring in copper deposited through the use of its more complicated superfilling electrolyte. Summarizing, this first major increment of work from NIST provided the first published account linking fully disclosed electrolyte chemistry with the superfilling and recrystallization behaviors required for successful damascene processing.

Insight derived from the above first publication led to new research findings and a series of subsequent publications, including those by Moffat et al. (2001); Josell, Wheeler, Huber, and Moffat (2001); and Wheeler, Josell, and Moffat (2003), which presented a quantitative competitive adsorption model, known as the CEAC model, that explained the key features of the superfilling phenomenon. Two key mathematical equations in the CEAC model allowed kinetic parameters, derived from electrochemical measurements of deposition rates taken from any electrolyte on a planar substrate, to be used to predict quantitatively the shape change that accompanies copper plating on 3-D patterned or any nonplanar surfaces. The model provided a straightforward, physically

⁴ Hysteresis is broadly defined as a system that has memory and in which future change depends on the past. Wikipedia offers a discussion of hysteresis, including several diagrams and links to additional research at <http://en.wikipedia.org/wiki/Hysteresis>.

robust explanation of the superfilling process. This included quantitative prediction of the characteristics of three key parameters (the incubation period, bottom-up filling, and overflow bump formation) observed experimentally during trench filling.

Prior to publishing the third of the three papers that provided increasing numerical sophistication to the CEAC model specification, a fourth paper by Josell, Wheeler, Huber, Bonevich et al. (2001) presented an approximation of the key equations in the previous papers that enabled theoretical exploration of superfilling behavior over a wide range of experimental parameters. This tool enabled an evaluation and optimization of the processing conditions for feature filling in a fraction of the computational time then required to produce an exact solution. Similar measurements and modeling were subsequently extended to address the geometry of vias (Josell, Wheeler, and Moffat, 2002; Josell et al., 2002).

NIST also wrote and published open-source software code and wrote accompanying instructions and other documentation for the industry to more easily use its model. At first, NIST developed a basic “string model” solution, and then “level set” code that could be more easily adopted but still required the Physica platform.⁵ Finally, it developed a more usable version called FiPy. FiPy is an object-oriented, partial differential equation solver, written in Python, based on a standard finite-volume approach. FiPy includes algorithms for phase field and level set interface motion. First released in November 2004, the FiPy code and the documentation are available on NIST’s Web site.⁶

NIST continued to conduct research on superfilling and published a number of additional findings over the next 5 years (see Appendices A, B, and C for more details on NIST’s findings and lists of related papers and presentations). NIST helped leverage the superfilling process for use in achieving future technology nodes with smaller feature sizes. Further, the NIST group has been an important player in researching issues related to direct copper superfilling on seed and barrier layers beyond

⁵ Physica is a high-level, interactive programming environment with user-friendly graphics and sophisticated mathematical analysis capabilities. EXTREMA is the name of the newest version of Physica, which now includes a full-featured graphical user interface. See <http://exsitewebware.com/extrema/index.html>.

⁶ The Web page for the main code “FiPy” is <http://www.ctcms.nist.gov/fipy/>. The instructions for downloading the code are at <http://www.ctcms.nist.gov/fipy/installation.html>. The manual is available at <http://www.ctcms.nist.gov/fipy/download/fipy.pdf>. A specific example of how to use the code to solve the level-set electrochemistry problem is given in Section 8.5 of the manual.

conventional copper substrates.⁷ And the generality and predictive power of NIST's CEAC model have been demonstrated by extension to other material systems (e.g., silver [Ag] and gold [Au]), as well as to other deposition technologies such as chemical vapor deposition (CVD). The utility of the CEAC model in extending and optimizing the copper superfilling process and its application to other materials systems are certain to be an important component of future technological developments (Moffat, Baker, et al., 2002; Baker, Freeman et al., 2003; Baker, Witt, 2003; Josell et al., 2005; Josell, Wheeler, and Moffat, 2006).

In summary, the CEAC model, conceived and quantified by NIST, provided a means for quantitative prediction of the ability of alternate chemical additives to induce optimal superfilling. Industry segments potentially affected by this advancement include chemical and material suppliers, equipment suppliers, and device manufacturers. The benefits to industry accrued in the form of reduced R&D costs associated with developing the next generation of ICs. Better predictive models reduced the need for trial-and-error processes and increased production yield rates.

Full use of the CEAC model allowed identification of the optimal experimental parameters for void- and seam-free feature filling with minimal overfilling principally through rapid, inexpensive studies on planar substrates and CEAC modeling rather than exhaustive, costly feature-filling studies. NIST's work enabled the following:

- more rapid screening of electrolyte systems for interconnect fabrication applications that accelerated implementation;
- quantitative prediction of electrolytes' efficacy that substantially reduced the time and effort involved in experimental fill studies for implementation in applications;
- improved processing through predictive understanding of the superfilling mechanism, including incubation period, bottom-up filling, and overfill bump formation; and
- extrapolation of existing results to more advanced (e.g., smaller) dimensions even prior to the availability of industrial patterned wafers with such filling geometries.

⁷ NIST has published fully detailed accounts demonstrating copper superfilling on ruthenium (Ru), osmium (Os), and iridium (Ir) seed/barrier layers prepared by a variety of means (physical vapor deposition [PVD], chemical vapor deposition [CVD], and atomic layer deposition [ALD]). See Josell et al. (2003); Josell et al. (2006); Josell, Witt, and Moffat (2006); and Moffat, Walker et al. (2006). Likewise, three papers report extensively on the process control challenges of direct plating on Ru that have been the focus of most industrial interest in this area (Josell et al., 2003; Moffat, Wheeler et al., 2006; Walker et al., 2006). NIST's work on Ru resulted in an invited contribution to Semiconductor Fabtech, detailing the challenges and future opportunities provided by a seedless superfilling process (Moffat and Josell, 2005).

3

Quantitative Analysis

RTI estimated the net economic benefits (private and social) accruing from NIST's research investment in superfilling characteristics and modeling. RTI focused specifically on the initial development of NIST's CEAC model, the major aspects of which were first disseminated in the research community through seven published papers. These hallmark papers (in parentheses), written based on research conducted between 1999 and 2002, accomplished the following:

- linked hysteresis and bottom-up filling of trenches during copper deposition (Moffat et al., 2000);
- described the equations that make up the CEAC model (Moffat et al., 2001; Josell, Wheeler, Huber, and Moffat, 2001; Wheeler, Josell, and Moffat, 2003);
- demonstrated how the CEAC equations could be used to drastically increase the evaluation efficiency of key processing parameters (e.g., the incubation period, the shape and process of bottom-up filling, and overfill bump formation) (Josell, Wheeler, Huber, Bonevich et al., 2001); and
- discussed how the expanded model could be used to predict the effects of changes in geometry (Josell, Wheeler, and Moffat, 2002; Josell et al., 2002).

Together, these papers provided the fundamental body of knowledge necessary for the semiconductor industry to adopt and benefit from using the CEAC model. This body of knowledge is the focus of this study.

3.1 ESTABLISHING THE PERIOD OF ANALYSIS

The focus of the analysis was on the adoption and use of research knowledge and techniques concerning the CEAC model as reflected through the seven hallmark papers referenced above, beginning with Moffat et al. (2000) and culminating in the publication by Wheeler, Josell,

and Moffat (2003). Costs were estimated for research, conducted between 1999 and 2002, that resulted in these papers.

Benefit estimates for each application phase of use of NIST's research findings—in R&D, in the adoption of superfilling, and in production—were considered, but as discussed below, R&D cost savings were the only benefit that could be quantified. Interviews suggested that benefits accrued to stakeholders between 2003 and 2005.

3.2 IDENTIFYING AFFECTED STAKEHOLDERS

As discussed in Chapter 2, NIST's research affected the industry by significantly improving the superfilling process and reducing R&D costs. More specifically, the following industry groups were/are affected:

- *Chemical and Material Suppliers:* Within this group, the three main electrolyte suppliers in the United States were/are Rohm and Haas, Cookson Electronics-Enthone Inc., and DuPont. Cookson Electronics-Enthone dominates the market today, but all benefited from NIST's research findings.
- *Equipment Suppliers:* Manufacturers of superfilling equipment (i.e., electroplating equipment) were the main equipment suppliers affected. The major companies involved in producing electroplating equipment in the United States were/are Semitool and Novellus. Applied Materials and Nexx are other suppliers.
- *Analytical Tool Suppliers:* Companies that develop tools to help with analysis of process parameters in process or in R&D phases include NuTool, ECI Technology, and Technic.
- *Device Manufacturers:* R&D within manufacturers of ICs and related devices was the functional area most affected by NIST's findings. Manufacturers' R&D was critical to production remaining at the state of the art, which required using copper in ICs. In general, any manufacturer filling high aspect ratio vias with copper during our period of analysis certainly benefitted from its R&D in that area. The main U.S. manufacturers likely to have R&D facilities capable of using NIST's findings were/are IBM, Motorola, AMD, Intel, and TI.

Table 3-1 displays descriptive employment and sales information for the main companies in each stakeholder group that were or are involved to some extent in copper superfilling.

The four groups noted in Table 3-1 represent what could also be referred to as the superfill supply chain. With the assistance of Josell and Moffat at NIST, efforts were made to identify an individual at each company who

Table 3-1. Major Stakeholders' Total Sales and Employment Data, by Company

Company	Company Sales (2007 \$million)	Employment
Chemical and Material Suppliers		
Cookson Electronics-Enthone ^a	\$2,315	14,074
Rohm and Haas ^b	\$8,897	15,710
Dupont	\$30,653	60,000
Dow Chemical	\$53,513	45,856
Equipment Suppliers		
Novellus	\$1,570	3,698
Semitool	\$215	1,157
Applied Materials	\$9,735	15,328
Nexx	\$3	38
Analytical Tool Suppliers		
NuTool	\$11,407 ^c	11,832 ^c
ECI Technology ^d	\$8	65
Technic	\$60	425
Device Manufacturers		
Intel	\$38,334	86,300
AMD	\$6,013	16,420
IBM	\$98,786	426,969
TI	\$13,835	30,175

^a Cookson Electronics acquired Enthone, a major chemical supplier, in 1999;

^b Rohm and Haas acquired Shipley, a major chemical supplier, in 1999;

^c Employment and sales figures reported for NuTool are for its parent company, ASM International;

^d ECI Technology is also a supplier of chemicals and materials for copper superfilling.

could speak to the impact of the CEAC model and who would be willing to talk with RTI about dimensions of the economic impact of the model. Representatives of 11 companies were willing to participate in RTI's data collection efforts. These companies span all elements of the supply chain: two chemical suppliers, two equipment suppliers, three analytical tool suppliers, and four device manufacturers. Table 3-2 provides approximate estimates of the market coverage represented by the information collected during interviews. The "market" was estimated during interviews as the portion of companies' sales relevant to superfilling chemicals, equipment, or tools (for chemical and material suppliers, equipment suppliers, and analytical tools suppliers) and the portion of device manufacturer products that use copper for interconnect, and hence use a superfilling process during manufacturing.

Table 3-2. Market Coverage of Relevant Stakeholders through Interviews

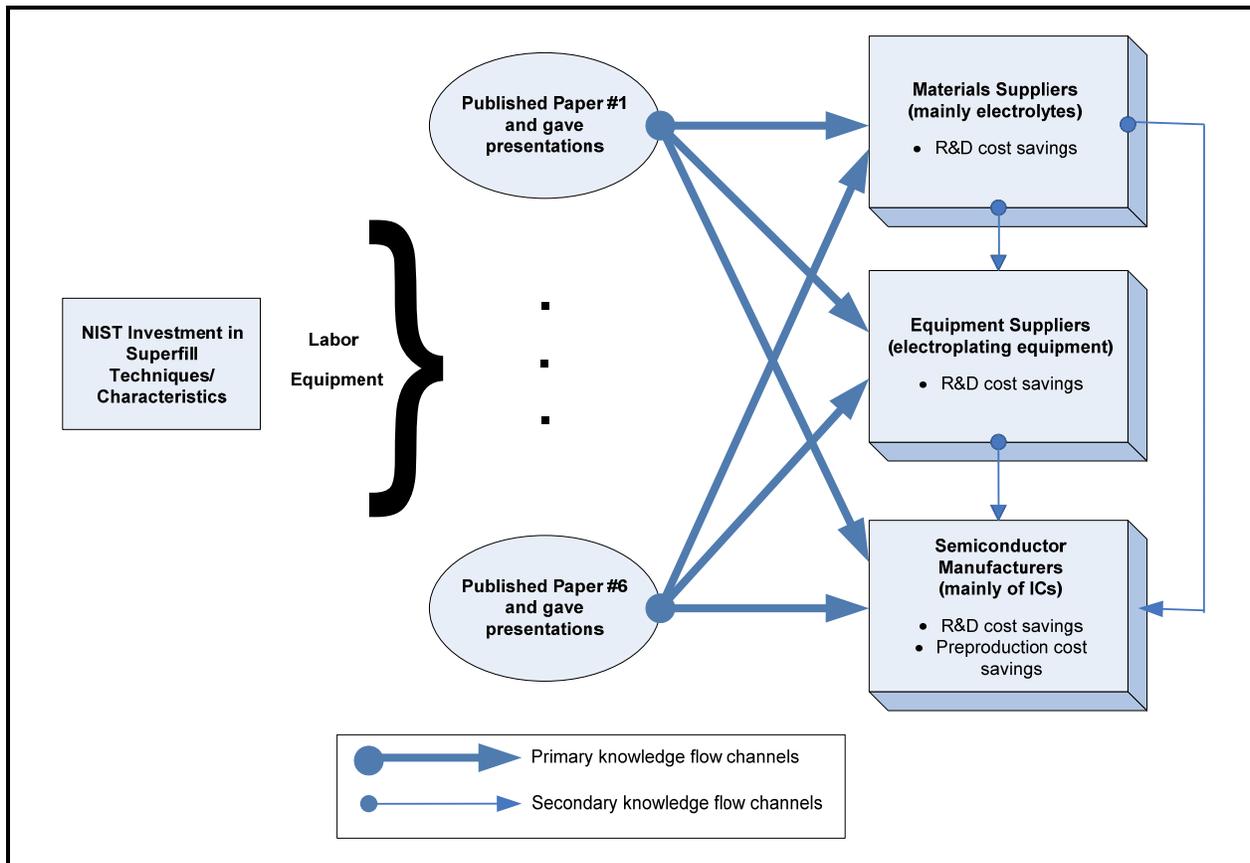
Stakeholder Group	Number of Firms	Approximated Market Share Represented by Sample Firms
Chemical and Material Suppliers	2	85%
Equipment Suppliers	2	80%
Analytical Tool Suppliers	3	50%
Device Manufacturers	4	80%

3.3 THE COUNTERFACTUAL EVALUATION METHOD

The counterfactual evaluation method is the appropriate method for evaluating a publicly funded, publicly performed research project. NIST's research on superfilling clearly fits in this domain. The evaluation question asked when using the counterfactual evaluation method is: What would the private sector have done in the absence of the public sector's research funding support? The answer to this question gives the benefits of the public's investments—namely, the costs saved or avoided by the private sector. This approach also seeks to determine whether the publicly funded research provided a unique capability or a result otherwise not possible or likely to occur (i.e., because private entities would not have been able to see a sufficiently positive private return on investment).

Figure 3-1 conceptualizes the knowledge flows associated with NIST's research on superfilling. The figure illustrates the primary (bolder lines of impact) and secondary impacts of NIST's research as disseminated through the seven hallmark papers discussed above. The figure also notes explicitly several categories of benefits that conceptually were obtained from the CEAC model and the related papers; the counterfactual evaluation method was used to determine the costs avoided by companies in the industry to replicate these categories of benefits.

Figure 3-1. Primary and Secondary Knowledge Flows of NIST Superfilling Research



According to industry and expert interviews, NIST's research significantly altered the knowledge base and predictive capabilities of R&D within the industry related to the superfilling process. Although a handful of organizations were conducting research on superfilling characteristics and electrolyte properties when NIST first became directly involved in this research in 1999, prior to NIST's research and publications, the industry's R&D infrastructure was operating under several inaccurate assumptions regarding the superfilling process. As a result, the industry could not predict how to achieve optimal superfilling results. Progress by scientists outside NIST varied, but, according to industry stakeholders interviewed by RTI, all lagged significantly with regard to improving the predictive knowledge of the superfilling process relative to NIST's contributions.

As an example, 1 year after NIST researchers published their first paper demonstrating the relationship between superfilling electrolyte properties and hysteresis (Moffat et al., 2000) and began describing the link in

public presentations, the industry had not fully accepted their findings. Models by non-NIST researchers (e.g., West, Mayer, and Reid, 2001) noted hysteresis but incorporated initial (equilibrium) conditions that were inconsistent with NIST's work. This illustrates the seminal nature of NIST's findings.¹

Through interviews with industry, RTI confirmed that in the absence of NIST's research—as codified through the seven hallmark papers and the CEAC model—the direct beneficiaries of NIST's work (or their sponsors and/or the academic community, either domestically or internationally) would have conducted superfilling research on their own. However, this industry focuses on the most efficient R&D activities; RTI's research suggests that very few companies (i.e., IBM and possibly Motorola and AMD) would have undertaken such in-depth research as NIST did into the infratechnologies that enable new or improved R&D and preproduction processes. Moreover, academic researchers working on superfilling were not expending the same level of resources as NIST did. Consequently, NIST's research findings likely would not have been discovered by other company or academic researchers for at least 2 to 3 years.

3.4 RESEARCH COSTS AND QUANTIFIED PRIVATE-SECTOR BENEFITS

Josell and Moffat at NIST estimated NIST's costs between 1999 and 2002 to undertake the research that culminated in the CEAC model described in the seven hallmark papers noted above (i.e., research costs associated with copper electrodeposition). These costs, in nominal dollars and in real 2008 dollars, are reported in Table 3-3. The values in Table 3-3 include fully burdened labor (salary plus benefits), chemicals and materials costs, equipment costs, and overhead.

As discussed above, the counterfactual evaluation method considers the private sector's benefits, and hence society's benefits, to be the research costs avoided by the private sector had it invested sufficiently to achieve the same product specifications without NIST. In other words, the evaluation question related to benefits is: What would industry have done without the body of knowledge developed by NIST as discussed in the

¹ Alan West at Columbia and Steven Mayer and Jonathan Reid at Novellus are three of the most well-known researchers who were working on superfilling during the period of analysis.

Table 3-3. NIST Research Costs Relating to Superfilling (\$nominal and \$2008)

Year	Nominal Cost	Real Cost (\$2008)
1999	\$230,000	\$287,500
2000	\$340,000	\$414,634
2001	\$331,000	\$394,048
2002	\$324,000	\$381,176
Total	\$1,225,000	\$1,477,358

Note: Real (\$2008) costs were calculated using the seasonally adjusted Gross Domestic Product Implicit Price Deflator (2000=100), U.S. Department of Commerce: Bureau of Economic Analysis, <http://research.stlouisfed.org/fred2/data/GDPDEF.txt>.

seven hallmark papers referenced above and embodied in the CEAC model? This is precisely the question RTI asked each representative of each company interviewed in this study.

Prior to the interview, each representative who participated in our interviews was provided with an annotated list of the seven hallmark papers to ensure a common understanding of the NIST-generated body of knowledge under study. Each representative was asked to respond to the cost-savings question in terms of the number of full-time equivalent (FTE), fully burdened scientists who would have been needed within the company to replicate NIST's research.

RTI prepared and used an interview guide to facilitate the interviews (see Appendix D). Generally, participants were unable to provide quantitative information on benefits beyond R&D cost savings. This was not because of the complexity of the questions, but rather because of both (1) the difficulty involved in recalling the specific use of NIST's contributions by researchers and (2) the complexity involved in tracing the impact of a new research model downstream beyond R&D activities. Interview participants did discuss qualitatively additional benefits, which are discussed in the concluding remarks in Chapter 5.

Table 3-4 summarizes the responses for 11 companies whose representatives were interviewed regarding the accrual benefits from NIST's work. Interview participants provided information on the R&D cost savings or costs avoided in 2008 dollars as a result of the body of knowledge embodied in the CEAC model and in the seven hallmark papers. As discussed previously, most companies were not conducting research that would have resulted in the discovery of NIST's research

Table 3-4. Private-Sector R&D Cost-Savings Benefits: Base Case (\$2008)

Year	Cost-Savings Benefits
2003	\$1,920,000
2004	\$1,920,000
2005	\$1,110,000
Total	\$4,950,000

Note: Based on interview information. The lower cost-savings estimate for 2005 reflects the assertion by some company representatives that it would have taken their company 2.5 years (i.e., between 2 and 3 years) rather than 3 years to replicate NIST's findings.

findings. Thus, the R&D and preproduction cost savings resulting from NIST's involvement most clearly could be defined as additional R&D costs that companies would have incurred absent NIST's research and the resulting model.

The "base case" estimate of almost \$5,000,000 includes benefits that RTI quantified directly through interviews. Estimates of the benefits of NIST's research were also extrapolated to the entire industry, and the resulting figures are presented in Chapter 4.

The values in Table 3-4 reflect the time period deemed to have been required to replicate NIST's research results. Generally, representatives reported that, beginning in 2003, there would have been a 2- to 3-year lag before another organization would have developed the CEAC model.

3.5 ADDITIONAL NONMONETARY BENEFIT METRICS

In addition to the reported cost savings or costs avoided that RTI estimated based on information provided during interviews with company representatives, RTI collected qualitative information relevant to the social benefits associated with NIST's research. RTI calculated the number of nonauthor citations to each of the seven hallmark publications listed above to illustrate one dimension of the spillover impact of NIST's research. Citation counts, year-by-year and cumulative, are provided in Table 3-5. By 2008, these seven papers had been cited over 250 times by other researchers in peer-reviewed journal articles. In addition,

Table 3-5. Nonauthor Citations to the Seven Hallmark Papers, by Year

Year	Number of Papers Published (Month of Publication)	Citations	Cumulative Citations
2000	1 (December)	0	0
2001	3 (July, August, and December)	6	6
2002	2 (April, December)	13	19
2003	1 (May)	48	67
2004		51	118
2005		44	162
2006		50	212
2007		37	249
2008		10	259

Note: Citations in 2008 are through April 21.

several patents and patent applications also cite these papers as important knowledge on which their ideas were based.²

As discussed in Chapter 2, NIST researchers also developed software code to enable the industry to use the CEAC model more easily. NIST's FiPy open-source software was available on its Web site, along with documentation and instructions. Combined with its publications, NIST's software provided yet another way for the industry to benefit from NIST's research findings. Between 2003 and 2004, at least seven companies³ requested the code directly from NIST, and likely many more used the information on its Web site.⁴

² This information is presented in Appendix E to illustrate the influence of that body of knowledge on downstream research.

³ Blue29, ST Microelectronics, ATMI, Intel, Maxim, 3M, and GM all requested the FiPy code and/or provided feedback to NIST regarding their use of NIST's FiPy software.

⁴ NIST does not track downloads from its Web site and thus was unable to estimate the number of organizations and individuals that have used its software code.

4

Measures of Economic Return

RTI calculated three traditional evaluation metrics relevant to this study: the benefit-to-cost ratio (BCR), net present value (NPV), and the internal rate of return (IRR). Each metric is discussed below conceptually, followed by a presentation of the results from this study.

4.1 EVALUATION METRICS DESCRIPTION

Benefit-to-Cost Ratio

To calculate the BCR, let B_t be the benefits accrued in year t by firms and C_t the total costs to produce those benefits in year t . In the case of superfilling, all costs were incurred by NIST during the years 1999 through 2002, and all measured benefits were realized in years 2003 through 2005.¹ The formulation for the BCR is as follows:

$$\text{BCR} = \frac{\sum_{i=0}^n \frac{B_{(t+i)}}{(1+r)^i}}{\sum_{i=0}^n \frac{C_{(t+i)}}{(1+r)^i}}, \quad (4.1)$$

where

t is the first year in which benefits or costs occur,

n is the number of years in which the benefits and/or costs occur, and

r is the real social rate of discount.

Following the Office of Management and Budget's (OMB's) recommended social rate of discount (OMB, Circular A-94, 1992), r was

¹ The adjective "measured" in reference to benefits denotes that industry realized other benefits from the NIST research on superfilling, but those benefits could not be quantified in this study. They are discussed in Chapter 5.

set at 7%. Because benefits and costs occur at different time periods, both are expressed in present-value terms before the ratio is calculated. Essentially, a BCR greater than 1 indicates that quantified benefits outweighed the calculated costs. A BCR less than 1 indicates that costs exceeded benefits, and a BCR equal to 1 means that the project broke even.

Net Present Value

The NPV of NIST's investment in superfilling as reflected in the CEAC model through the seven hallmark publications is calculated as follows:

$$NPV = \sum_{i=0}^n \left[\frac{B(t+i)}{(1+r)^i} - \frac{C(t+i)}{(1+r)^i} \right], \quad (4.2)$$

where the terms were defined in reference to equation (4.1) above. Any project that yields a positive NPV is considered economically successful. Projects that reveal a positive NPV when analyzed using OMB's 7% real social rate of discount are generally interpreted to be or to have been socially advantageous. A negative NPV would indicate that the costs to society outweigh the benefits, and an NPV equal to zero would indicate a break-even point.

Internal Rate of Return

The IRR on NIST's investment in superfilling can broadly be interpreted as the percentage yield to society on a publicly funded project over the life of the project (Tassey, 2003). Mathematically, the IRR is the value of r that sets the NPV equal to zero in equation (4.2), or results in a BCR of 1 in equation (4.1).

The IRR's value can be compared with conventional rates of return for comparable or alternative investments. Risk-free capital investments such as government bonds can be expected to yield rates of return under 5% in real terms, whereas equities seldom return more than 10% over an extended period of time. In academic studies of the diffusion of new technologies, however, real rates of return of 100% or more have been found for significant advances with broad social benefits.

4.2 EVALUATION ANALYSIS AND RESULTS: BASE CASE AND EXTRAPOLATED CASES

Table 4-1 is a summary of the real cost data in Table 3-3 and the interview benefit data in Table 3-4. The data in Table 4-1 are the basis for the calculations of the evaluation metrics in Table 4-2. Based on data collected explicitly during interviews, NIST's research resulted in net benefits of \$3,472,642 with an NPV of \$2,242,994. The benefit-to-cost ratio is 2.69, and the internal rate of return is 43.4%.

Table 4-1. NIST Research Costs and Private-Sector R&D Benefits: Base Case (\$2008)

Year	Real Cost	Real Cost-Savings Benefits
1999	\$287,500	\$0
2000	\$414,634	\$0
2001	\$394,048	\$0
2002	\$381,176	\$0
2003	\$0	\$1,920,000
2004	\$0	\$1,920,000
2005	\$0	\$1,110,000
2006	\$0	\$0
2007	\$0	\$0
Total	\$1,477,358	\$4,950,000
NPV	\$1,330,339	\$3,573,332

Table 4-2. Evaluation Metrics: Base Case

Metric	Value
Costs (\$2008)	\$1,477,358
Benefits (\$2008)	\$4,950,000
Net Benefits (\$2008)	\$3,472,642
Benefit-to-Cost Ratio (BCR)	2.69
Net Present Value (NPV) (\$2008)	\$2,242,994
Internal Rate of Return (IRR)	43.4%

The evaluation information in Tables 4-1 and 4-2 is based on the explicit assumption that all industry benefits are equal to the benefits realized by the 11 companies whose representatives RTI interviewed. Clearly, the market share information in Table 3-2 suggests that an extrapolation of benefits from the interviewed companies to the industry would be justified. If so, then the evaluation metrics in Table 4-2 are lower-bound estimates. Still, these conservative evaluation estimates indicate that, from a social perspective, NIST's investments in superfilling research were worthwhile.

To place these evaluation estimates in a broader context, RTI extrapolated the industry benefits shown in Table 4-1 in two ways (see Table 4-3). First, RTI used a full extrapolation (e.g., if the cost-savings benefits to companies that represent 75% of the market of equipment suppliers are \$X, then cost-savings benefits to equipment suppliers would be $\$X/.75$) as shown in column 4 of Table 4-3. Second, RTI used a 50% extrapolation (i.e., the average of the benefits in columns 3 and 4 of Table 4-3). The corresponding evaluation metrics are provided in Table 4-4.

The two alternative cases provide more probable metrics by which to gauge the cost-savings impact of NIST's investments. Based on interviews with industry, RTI believes that providing a lower-bound estimate and an upper-bound estimate is the most accurate way to display the range of potential benefits estimates. This range reflects the fact that we were not able to interview all companies conducting superfilling R&D and that extrapolating expenditures on complex R&D activities based on a sample of interviews is not as simple as extrapolating estimates of other more routine R&D activities.

The full extrapolation resulted in calculated net benefits of \$9,249,112 and an NPV of \$6,428,697. The BCR check was 5.83, and the IPR 79.4%. The partial (50%) extrapolation is a more conservative estimate of the cost-savings benefits accrued by the industry. The partially extrapolated net benefits were \$6,360,877 with an NPV of \$4,335,845. The BCR for the partial extrapolation was 4.26, and the IRR was 64.0%.

Table 4-5 provides benefits by stakeholder group. As the table shows, device manufacturers received the majority of the benefits with more than \$6,000,000 accrued. This result is expected; interviews suggested that manufacturers were spending the most time trying to solve the issue of superfilling and would have conducted any research needed

Table 4-3. NIST Research Costs and Private-Sector R&D Benefits: Base Case and Extrapolated Cases (\$2008)

Year	Real Cost	Real Cost-Savings Benefits	Real Cost-Savings Benefits: Fully Extrapolated	Real Cost-Savings Benefits: 50% Extrapolated
1999	\$287,500	\$0	\$0	\$0
2000	\$414,634	\$0	\$0	\$0
2001	\$394,048	\$0	\$0	\$0
2002	\$381,176	\$0	\$0	\$0
2003	\$0	\$1,920,000	\$3,643,333	\$2,781,667
2004	\$0	\$1,920,000	\$3,643,333	\$2,781,667
2005	\$0	\$1,110,000	\$1,762,500	\$1,511,250
2006	\$0	\$0	\$0	\$0
2007	\$0	\$0	\$0	\$0
Total	\$1,477,358	\$4,950,000	\$10,726,471	\$7,838,235
NPV	\$1,330,339	\$3,573,332	\$7,759,035	\$5,666,184

Table 4-4. Evaluation Metrics: Base Case and Extrapolated Cases

Metric	Value Based on Interview Data	Value Based on Full Extrapolation of Benefits	Value Based on 50% Extrapolation of Benefits
Costs (\$2008)	\$1,477,358	\$1,477,358	\$1,477,358
Benefits (\$2008)	\$4,950,000	\$10,726,471	\$7,838,235
Net Benefits (\$2008)	\$3,472,642	\$9,249,112	\$6,360,877
Benefit-to-Cost Ratio	2.69	5.83	4.26
Net Present Value (\$2008)	\$2,242,994	\$6,428,697	\$4,335,845
Internal Rate of Return	43.4%	79.4%	64.0%

Table 4-5. R&D Benefits Estimates by Stakeholder Group (\$2008)

Stakeholder Group	Value Based on Full Extrapolation of Benefits
Chemical and Material Suppliers	\$1,800,000
Equipment Suppliers	\$1,676,471
Analytical Tool Suppliers	\$1,000,000
Device Manufacturers	\$6,250,000
Total	\$10,726,471

to stay on track with the Roadmaps. Chemical and material suppliers and equipment suppliers both received more than \$1.5 million in benefits, and analytical suppliers received approximately \$1 million in benefits. Working in supportive roles to the device manufacturers, each of these groups would have made additional R&D investments to stay competitive in the absence of NIST's research.

5

Conclusions

In this study, RTI quantified the impact of NIST's superfilling program on the R&D portion of the semiconductor industry. The values of the evaluation metrics in Table 4-4 clearly indicate that NIST's investments in superfilling, as reflected by the seven hallmark papers that introduced the CEAC model, have had a significant positive social return.

The fully extrapolated benefits calculation shows that NIST's investments resulted in more than \$9 million of net benefits and an NPV of almost \$6.5 million. These calculations represent what the industry would have spent in the absence of NIST's research and findings less NIST's costs. Industry stakeholders indicated that they would have invested the funds necessary to test additives' properties for superfilling suitability individually by trial and error in order to achieve the product goals set forth by the industry's Roadmaps. Stakeholders benefited by not having to conduct such comparatively inefficient analyses. Further, some stakeholders, who were working to develop a model similar to NIST's, benefited by saving the cost of such research.

In fact, these values may be considered conservative for several reasons, even in the absence of the extrapolation of benefits, and thus may understate the social benefits associated with NIST's research in superfilling. Below we provide an analysis of additional, nonquantified benefits stemming from NIST's research, as well as some observations for NIST.

Additional quantitative analysis related to the benefits of using NIST's research findings on, for example, preproduction and production activities was not possible. Relevant information was not documented by

industry in “real time” when NIST research and results were being used; thus, industry members could not estimate more complex benefits.

5.1 ADDITIONAL BENEFITS

RTI's research suggests that the benefits from NIST's research go well beyond those quantified in this report. However, both the time that has elapsed since NIST's research was published and the difficulty involved in attributing benefits beyond R&D cost savings to new R&D research methods made accurately quantifying additional benefits very difficult.

The use of NIST's research results occurred approximately 7 years ago; hence, many researchers were unable to accurately recall the exact use and benefits of NIST's research findings. Although RTI's benefit estimates are truncated at 2005, it is possible that the interview participants were overly optimistic about their companies' abilities to replicate NIST's results (with the benefit of hindsight), and even more so in their ability to do so within 2 to 3 years.

Further, as discussed throughout this report, R&D cost savings are just one of the components of the cost savings that resulted from NIST's knowledge flow chain (see Figure 3-1); however, estimating additional benefits proved impossible for interview participants.

5.1.1 Preproduction and Production Cost Savings

As successful R&D finds its way into production, production cost savings result. Device manufacturers, however, were unable to quantify impacts such as decreasing preproduction costs or accelerating the transition to production.

According to our interviews, significant cost savings resulted from NIST's research in the form of increased preproduction efficiency for second-generation ICs. Prior to full production of a new product, preproduction activities focus on improving yield—the percentage of produced chips achieving the quality threshold necessary for sale to customers. NIST's work accelerated this preproduction process for the second generation of ICs that used copper for interconnects. Thus, manufacturers were able to develop higher-quality chips faster, thus reducing overall production costs and accelerating the market availability of the second generation of ICs that used copper.

Companies began producing and selling ICs with copper interconnects as early as September 1998, with IBM being the first to test and put

copper ICs on the market (Edelstein et al., 1997; Lim, 2008).¹ Many companies were able to ship first-generation products without the knowledge generated by NIST researchers. Manufacturers were able to achieve the necessary level of quality to ship new 180 nm chips to customers by conducting trial-and-error testing of electrolyte chemical composition.²

However, once companies focused on developing ICs at subsequent technology nodes, 150 nm and below, the difficulty in achieving desirable filling characteristics increased significantly. At aspect ratios of greater than approximately 2.5 and for smaller lateral dimensions of vias and trenches, pores (voids) were much more likely to develop during the dual damascene copper filling process. Our interviews suggest that without NIST's model manufacturers could have lost significant efficiency in their preproduction processes, adding costs and slowing the availability of new products.

With respect to the next stage of the knowledge flow, namely production, neither R&D researchers nor their colleagues who are directly involved in manufacturing were able to identify benefits such as cost savings or additional product quality resulting explicitly from NIST's research. In general, IC production activities are far removed in the knowledge flow chain from the point of origin of research and are a complex function of such a large number of individual research outcomes that tracking and quantifying impacts of a specific research activity are speculative at best.

5.1.2 Information Exchange and Objectivity

Interview participants discussed several even less tangible forms of economic benefits. For example, equipment suppliers noted that the CEAC model gave them the ability to explain to customers in an understandable way what a company's tool could do, which helped the company retain its customer base and, more importantly, helped convince its customers to adopt NIST's findings. The NIST "assurance" was cited as a very important part of NIST's involvement by other

¹ Motorola released its own product using copper technology approximately 8 months later (mid-1999), followed by AMD's release in mid-2000. Texas Instruments and AT&T (now Lucent) came out with copper-based chips in 2001, and Intel in 2002. Several other non-U.S. companies came out with copper-based chips in 1999 and 2000. See Table 2 in Lim (2008) for estimates of the year of first shipment of chips with copper interconnect technology by all major semiconductor device manufacturers.

² According to manufacturers who participated in our interviews, the first generation of chips that included copper interconnects had a small aspect ratio for vias and trenches, around 2.2; as a result, understanding the exact relationships between the chemical properties of electrolytes and the superfilling process was not as important as it became later.

stakeholder groups as well. This benefit could not have been replicated by other companies, whose research findings would have been perceived as biased.

Further, several suppliers of superfilling equipment and superfilling additives indicated that NIST's involvement accelerated their product development cycles, and, hence, the release of products to semiconductor device manufacturers. In particular, one chemical supplier said that NIST's work allowed it to "develop chemistries intelligently for the first time." The NIST model provided guidelines to the industry as to the methodology for developing a production-grade superfilling process. As a result, manufacturers were able to demand more from chemical suppliers, who, with NIST's model, could now know more about the relationship between their products and customers' process parameters. However, interview participants were not able to quantify these benefits.

5.1.3 Accelerating Innovation and Future Benefits

The knowledge embodied in the CEAC model and in the seven hallmark papers influenced other scientists, as evidenced by the paper-citation information in Table 3-5 and by the patent citation information in Appendix E. This diffusion of knowledge certainly endowed benefits to society, but these qualitative benefits were not considered in the analysis above.

Further, NIST and industry have continued to build on the CEAC model since the publications that are the focus of this study. Appendix A discusses additional work by NIST researchers over the last 5 years, which was beyond the focus of this study. Interview participants suggested that the CEAC model is still very useful to the industry and likely will be for the foreseeable future.

5.2 OBSERVATIONS FOR NIST

During RTI interviews, participants were asked to offer feedback to NIST. Most expressed appreciation for NIST's distribution of its research findings through many venues—publishing papers, making presentations, and even sending researchers to specific companies to help them integrate NIST's findings. Although industry stakeholders involved in RTI's interviews generally believe that the industry would have developed the CEAC model findings in the absence of NIST, most credited NIST for providing a unique role by centralizing this research and quickly publishing the results for the entire industry to use.

6

References

- Andricacos, P.C. 1998. "Electroplated Copper Wiring on IC Chips." *Interface* 7(1):23-35.
- Andricacos, P.C., C. Uzoh, J.O. Dukovic, J. Horkans, and H. Deligianni. 1998. "Damascene Copper Electroplating for Chip Interconnections." *IBM Journal of Research and Development* 42:567-574.
- Baker, B.C., M. Freeman, B. Melnick, D. Wheeler, D. Josell, and T.P. Moffat. 2003. "Superconformal Electrodeposition of Silver from a KAg(CN)-KCN-KSeCN Electrolyte." *Journal of the Electrochemical Society* 150(2):C61-C66.
- Baker, B.C., C. Witt, D. Wheeler, D. Josell, and T.P. Moffat. 2003. "Superconformal Silver Deposition Using KSeCN Derivatized Substrates." *Electrochemical and Solid-State Letters* 6(5):C67-C69.
- Beaudry, C.L., and J.O. Dukovic. 2004. "Farady in the Fab: A Look at Copper Plating Equipment for On-Chip Wiring." *Interface* 13(4):40-44.
- Case, Chris. June 1, 2004. "Low-k Dielectrics: Was the Roadmap Wrong?" *Future Fab International, Section 6: Wafer Processing* Issue 17.
- Edelstein, D., J. Heindenrich, R. Goldblatt, W. Cote, C. Uzoh, N. Lustig, P. Roper, T. McDevitt, W. Motsiff, A. Simon, J. Dukovic, R. Wachnik, H. Rathore, R. Schutz, L. Su, S. Luce, and J. Slattery. 1997. "Full Copper Wiring in a Sub-0.25 μm CMOS ULSI Technology." *International Electron Device Meeting (IEDM) 1997 Technical Digest*, p. 773-776. Washington, DC.

- Horkans, J., and J.O. Dukovic. 2000. Paper provided in *Electrochemical Processing in ULSI Fabrication III* (from the 1997th Meeting of The Electrochemical Society, Toronto, Canada, May 14-18, 2000). P.C. Andricacos, P.C. Searson, C. Reidsema-Simpson, P. Allongue, J.L. Stickney, and G.M. Oleszek, eds. Volume 2000-8, p. 103, *the Electrochemical Society Proceedings Series*, Pennington, NJ.
- Josell, D., B. Baker, C. Witt, D. Wheeler, and T.P. Moffat. 2002. "Via Filling by Electrodeposition: Superconformal Silver and Copper and Conformal Nickel." *Journal of the Electrochemical Society* 149:C637-C641.
- Josell, D., C.R. Beauchamp, D.R. Kelley, C.A. Witt, and T.P. Moffat. 2005. "Gold Superfill in Sub-micrometer Trenches." *Electrochemical and Solid-State Letters* 8(3):C54-C57.
- Josell, D., J.E. Bonevich, T.P. Moffat, T. Aaltonen, M. Ritala, and M. Leskelä. 2006. "Iridium Barriers for Direct Copper Electrodeposition in Damascene Processing." *Electrochemical and Solid-State Letters* 9(2):C48-C50.
- Josell, D., D. Wheeler, W.H. Huber, J.E. Bonevich, and T.P. Moffat. 2001. "A Simple Equation for Predicting Superconformal Electrodeposition in Submicrometer Trenches." *Journal of the Electrochemical Society* 148:C767-C773.
- Josell, D., D. Wheeler, W.H. Huber, and T.P. Moffat. 2001. "Superconformal Electrodeposition in Submicron Features." *Physical Review Letters* 87(1):016102-1-016102-4.
- Josell, D., D. Wheeler, and T.P. Moffat. 2002. "Superconformal Electrodeposition in Vias." *Electrochemical and Solid-State Letters* 5:C49-C52.
- Josell, D., D. Wheeler, and T.P. Moffat. 2006. "Gold Superfill in SubMicrometer Trenches: Experiment and Prediction." *Journal of the Electrochemical Society* 153(1):C11-C18.
- Josell, D., D. Wheeler, C. Witt, and T.P. Moffat. 2003. "Seedless Superfill: Copper Electrodeposition in Trenches with Ruthenium Barriers." *Electrochemical and Solid-State Letters* 6(10):C143-C145.
- Josell, D., C. Witt, and T.P. Moffat. 2006. "Osmium Barriers for Direct Copper Electrodeposition in Damascene Processing." *Electrochemical and Solid-State Letters* 9(2):C41-C43.
- Kim, S.-K., D. Josell, and T.P. Moffat. 2006a. "Cationic Surfactants for the Control of Overfill Bumps in Cu Superfilling." *Journal of the Electrochemical Society* 153(12):C826-C833.

- Kim, S.-K., D. Josell, and T.P. Moffat. 2006b. "Electrodeposition of Copper in the PEI-PEG-CI-SPS Additive System, Reduction of Overfill Bump Formation during Cu Superfilling." *Journal of the Electrochemical Society* 153:C616-C622.
- Lim, K. 2008. "The Many Faces of Adsorptive Capacity: Spillovers of Copper Interconnect Technology for Semiconductor Chips." University of Melbourne Business School Working Paper. Available at <http://works.bepress.com/kwanghui/4/>.
- Moffat, T.P., B. Baker, D. Wheeler, J.E. Bonevich, M. Edelstein, D.R. Kelly, L. Gan, G.R. Stafford, P.J. Chen, W.F. Egelhoff, and D. Josell. 2002. "Superconformal Electrodeposition of Silver in Submicron Features." *Journal of the Electrochemical Society* 149(8):C423-C428.
- Moffat, T.P., B. Baker, D. Wheeler, and D. Josell. 2003. "Accelerator Aging Effects during Copper Electrodeposition." *Electrochemical Solid State Letters* 6(4):C59-C62.
- Moffat, T.P., J.E. Bonevich, W.H. Huber, A. Stanishevsky, D.R. Kelly, G.R. Stafford, and D. Josell. 2000. "Superconformal Electrodeposition of Copper in 500-90 nm Features." *Journal of the Electrochemical Society* 147:4524-4535.
- Moffat, T.P., and D. Josell. 2005. "Seedless Superfilling: Opportunities and Challenge." *Semiconductor FabTech* 27:133-136.
- Moffat, T.P., M. Walker, P.J. Chen, J.E. Bonevich, W.F. Egelhoff, L. Richter, C. Witt, T. Aaltonen, M. Ritala, M. Leskelä, and D. Josell. 2006. "Electrodeposition of Cu on Ru Barrier Layers for Damascene Processing." *Journal of the Electrochemical Society* 153(1):C37-C50.
- Moffat, T.P., D. Wheeler, M. Edelstein, and D. Josell. 2005. "Superconformal Film Growth: Mechanism and Quantification." *IBM Journal of Research and Development* 49:19-36.
- Moffat, T.P., D. Wheeler, W.H. Huber, and D. Josell. 2001. "Superconformal Electrodeposition of Copper." *Electrochemical and Solid-State Letters* 4:C26-C29.
- Moffat, T.P., D. Wheeler, and D. Josell. 2004a. "Electrodeposition of Copper in the SPS-PEG-CI Additive System: I. Kinetic Measurements: Influence of SPS." *Journal of the Electrochemical Society* 151:C262-C271.
- Moffat, T.P., D. Wheeler, and D. Josell. 2004b. "Superfilling and the Curvature Enhanced Accelerator Coverage Mechanism." *The Electrochemical Society Interface* 13(4):46-52.
- Moffat, T.P., D. Wheeler, S.-K. Kim, and D. Josell. 2006. "Curvature Enhanced Adsorbate Coverage Model for Electrodeposition." *Journal of the Electrochemical Society* 153:C127-C132.

- Moffat, T.P., D. Wheeler, S.-K. Kim, and D. Josell. 2007. "Curvature Enhanced Adsorbate Coverage Mechanism for Bottom-up Superfilling and Bump Control in Damascene Processing." *Electrochimica Acta* 53(1):145-154.
- Moffat T.P., D. Wheeler, C. Witt, and D. Josell. 2002. "Superconformal Electrodeposition Using Derivatized Substrates." *Electrochemical Solid State Letters* 5(12):C110-C112.
- Moore, G. 1965. "Cramming More Components onto Integrated Circuits." *Electronics Magazine* 38(8):114-117.
- Office of Management and Budget. 1992. "Circular No. A-94: Guidelines and Discount Rates for Benefit-Cost Analysis of Federal Programs," Washington, DC.
- Pavlov, M., E. Shalyt, P. Bratin, and D.M. Tench. 2003. "Detection of Accelerator Breakdown Products in Copper Plating Baths." In *Copper Interconnects, New Contact Metallurgies/Structures and Low-k Interlevel Dielectrics II*, G.S. Mathad et al., eds., pp. 53-62. The Electrochemical Society.
- Siegle, W. 2002. "Material Innovations Transform Mainstream Processor Design." *EETimes*.
- Tassey, G. 2003. *Methods for Assessing the Economic Impact of Government R&D*. NIST Planning Report 03-1. Gaithersburg, MD: NIST.
- Walker, M., L.J. Richter, D. Josell, and T.P. Moffat. 2006. "An Ellipsometric Study of the Cl-induced Adsorption of PEG on Ru and Cu UPD/Ru." *Journal of the Electrochemical Society* 153(4):C235-C241.
- West, A.C., S. Mayer, and J. Reid. 2001. "A Superfilling Model that Predicts Bump Formation." *Electrochemical Solid-State Letters* 4(7):C50-C53.
- Wheeler, D., D. Josell, and T.P. Moffat. 2003. "Modeling Superconformal Electrodeposition Using the Level Set Method." *Journal of the Electrochemical Society* 150:C302-C310.
- Witt, C., J. Srinivasan, and R. Carpio. 2004. "Influence of Leveling Agents on Surface Roughness of Electrodeposited Copper Films." In *Electrochemical Processes in ULSI and MEMS*, H. Deligianni, T.P. Moffat, S.T. Mayer, and G.R. Stafford, eds., pp. 57-66. The Electrochemical Society.
- Zuckerman, L. September 22, 1997. "IBM to Make Smaller and Faster Chips." *The New York Times*. Available at <http://query.nytimes.com/gst/fullpage.html?res=9C07E4DA143BF931A1575AC0A961958260>.

Appendix A: Additional NIST Superfilling Research Contributions

In addition to the research that is the focus of this study, NIST continued to conduct research into superfilling characteristics both on copper and on other materials such as silver and gold. To verify further the central tenets of the CEAC model, NIST explored a two-step process (Moffat, Wheeler et al., 2002) whereby the accelerator additive, mercaptopropene sulfonic acid (MPS) or bis (sodiumsulfopropyl) disulfide (SPS), was first adsorbed on the surface (derivatization) followed by feature filling in an electrolyte containing only a suppressor additive. This research was important in that it unambiguously demonstrated that accelerator surface chemistry, rather than homogeneous chemistry occurring in the electrolyte, was responsible for feature superfilling in contradiction to several other mechanistic studies under way (including at IBM) at the time. Implementation of the two-step process also enabled the incubation period of conformal growth to be eliminated, thereby allowing higher aspect ratio features to be filled. NIST was subsequently contacted multiple times by researchers from LAM Research (Dr. Yezdi Dordi) and Rohm and Haas (Dr. Craig Allen) who were looking into implementing the two-step process.

By breaking the superfilling process into two steps, the NIST work also helped clearly separate the dynamics of feature filling, per se, from the challenging and increasingly important manufacturing issue of process control and electrolyte aging effects. The latter were shown to arise from homogeneous chemistry occurring in the electrolyte between the SPS/MPS accelerator additive and copper ions that are generated at the counter electrode in the cell. By isolating the counter electrode from the

main cell using a cationic membrane, NIST (Moffat et al., 2003) was able to demonstrate significant stabilization of the process. Interestingly, this finding also contradicted some prior industrial reports (e.g., IBM) regarding electrolyte aging effects published in the literature (Horkans and Dukovic, 2000). Within a year or so of the NIST publication, all three major tool manufacturers—Applied Materials, Novellus, and Semitool—were offering plating tools with membrane-separated cells. NIST's contributions in this regard are well articulated in an article by Beaudry and Dukovic¹ (2004), a leading electrochemical cell design team at Applied Materials, as well as in a conference proceedings article (Pavlov et al., 2003) by researchers at the leading process control tool manufacturer, ECI.

NIST also used derivatization measurements to evaluate the kinetics of additive incorporation into the copper during deposition and permit their inclusion into feature filling dynamics. These measurements (Moffat, Wheeler, and Josell, 2004a; Moffat et al., 2005) provided a path to quantifying the surfactant character of the additives during metal deposition, thereby providing a further direct test of the central basis of the CEAC model as well as a screening tool for focused additive development and optimization. A strong potential dependence between the level of additive breakdown and incorporation in the metal deposits was noted and subsequently verified by industrial researchers (Witt, Srinivasan, and Carpio, 2004); incorporation of the additives and their breakdown products was an important parameter in the subsequent performance of copper metallization. Further measurements of this sort promise to provide the first link between electrochemical measurements of additive effects and the resulting effect of the additives on the microstructure.²

As damascene copper plating continued to make inroads into manufacturing, the overflow bump phenomenon associated with copper superfilling became a serious issue affecting yield during the subsequent chemical mechanical planarization (CMP) step. To overcome this problem, industry moved to using an additional additive in the electrolyte to quench the deposition rate immediately after feature filling but prior to

¹ John Dukovic, one of the authors of this paper, was formerly a key founding member of the IBM team that originally developed the copper superfilling process.

² NIST's work on the mechanism and quantification of superconformal films' growth in trench and via geometries is well summarized in two invited contributions published in the *IBM Journal of Research and Development* (Moffat et al., 2005) and the Electrochemical Society's quarterly *Interface* (Moffat, Wheeler, and Josell, 2004b), respectively.

the development of overfill bumps. As with the initial exploration of the superfilling phenomenon, industry began by approaching the problem using the traditional formalism of leveling to guide their exploration. In contrast, NIST researchers realized that the length scales associated with the actual filling process were inappropriate for a traditional leveling formalism, so instead they focused on building on the area change effect of the CEAC model to understand the action of the “leveler” addition. This resulted in the successful expansion of the CEAC model to include the effect of suppressor, accelerator, and inhibitors (referred to as “levelers” in the industry).

Two modeling papers detailing the effect of a three-component system on electrochemical transients and feature filling were published (Moffat et al., 2006; Moffat et al., 2007). Subsequent testing of the model has also resulted in the demonstration and full disclosure of two different electrolytes (Kim, Josell, and Moffat, 2006a; 2006b) that provided manufacturable solutions to the overfill bump problem. Most importantly, NIST’s CEAC model and measurement protocols have provided a firm foundation and rational basis for the further development and optimization of the superconformal feature filling process of importance to a variety of microsystem technologies.

Appendix B: NIST Superfilling Presentations/ Teaching

Between late 1999 and 2007, NIST researchers gave numerous invited and contributed presentations. These presentations, numbering approximately 80, were given at companies, universities, and society meetings, including at The Electrochemical Society (ECS) meetings, the Materials Research Society (MRS) meetings, the Advanced Metallization Conference (AMC), and the International Interconnect Technology Conference (IITC). NIST researchers presented invited talks at the following companies:

- Electrolyte suppliers: Shipley, Cookson Electronics, Rohm and Haas, and DuPont
- Tool makers: Applied Materials, and Semitool, Inc.
- Manufacturers: Intel and IMEC

Further, several NIST scientists spent time teaching companies NIST's techniques and conducting related research on site at companies. Daniel Wheeler, a NIST computational scientist, spent 6 months at Applied Materials helping their simulations group integrate the CEAC model. Brett Baker, after completing a postdoctoral position working with Thomas Moffat in NIST's Metallurgy Division of the Materials Science and Engineering Laboratory, joined the IBM T.J. Watson Research Center. Her work is focused on research issues related to electroplating copper.

The following is a list of invited presentations given by NIST researchers related to NIST's superfilling research (in reverse chronological order):

Superconformal Film Growth, Mechanism and Quantification, U.K. Basic Technology Consortium, November 7, 2007.

Superconformal Film Growth, Mechanism and Quantification,
Department of Materials Science, University of Virginia,
Charlottesville, VA, October 22, 2007.

Superconformal Film Growth, Mechanism and Quantification, Rohm and
Haas Electronic Materials, Marlborough, MA, December 1, 2006.

Superconformal Film Growth, Electrodeposition Division Research
Award Address, 210th Meeting of The Electrochemical Society
Meeting, Cancun, Mexico, November 1, 2006.

Superconformal Film Growth, Mechanism and Quantification, 34th ACS
Northeast Regional Meeting, Binghamton, NY, October 2006.

Superconformal Film Growth, Department of Materials Science,
Rensselaer Polytechnic Institute, Troy, NY, February 9, 2006.

Superconformal Film Growth, Science, Technology and Tools for
Electrodeposition from Lab to Factory, 208th Meeting of the
Electrochemical Society, Los Angeles, CA, October 19, 2005.

Superconformal Film Growth, Mechanism and Quantification,
International Symposium on Electrochemical Processing of
Tailored Materials, Kyoto, Japan, October 3, 2005.

Superconformal Film Growth, International Society of Electrochemistry,
Busan, Korea, September 26, 2005.

Superconformal Electrodeposition, DuPont Central R&D, Wilmington,
DE, July 27, 2005.

Electrodeposition of Cu on Ru Barrier Layers for Damascene
Processing, Symposium on Electrochemical Processing in ULSI
Fabrication and Electrodeposition of and on Semiconductors VI,
Quebec City, Canada, May 17, 2005.

Superconformal Film Growth, Department of Materials Science, The
Johns Hopkins University, Baltimore, MD, February 16, 2005.

Superconformal Film Growth, Semitool-Peaks in Plating Conference,
Whitefish, MT, September, 23, 2004.

Superconformal Film Growth, Cookson Electronics—Annual Corporate
Research Retreat, Providence, RI, July 15, 2004.

Superconformal Film Growth, Mardi Gras Conference at LSU, Baton
Rouge, LA, February 20, 2004.

Superconformal Film Growth, AIChE Topical Conference on
Electrodeposition in Microelectronics, AIChE Annual Meeting,
San Francisco, CA, November 2003.

Superconformal Film Growth, Characterization, Mechanistic Models and Transport Aspects of Cathodic and Anodic Processes, In Honor of Dieter Landolt, 204th Meeting of The Electrochemical Society, Orlando, FL, October 2003.

Superconformal Film Growth, Science and Application of Additives in Electrochemical Processes, 203rd Meeting of The Electrochemical Society, Paris, France, April 28, 2003.

Superconformal Film Growth, Princeton University, Institute of Materials Science, Princeton, NJ, April 8, 2003.

Superconformal Film Growth, Symposium on Copper Interconnects, New Contact Metallurgies and Low-K Dielectrics, ECS Fall Meeting, Salt Lake City, UT, October 20, 2002.

Superconformal Film Growth, Electrochemistry in Molecular and Microscopic Dimensions, 53rd Meeting of the International Society of Electrochemistry, Dusseldorf, Germany, September 18, 2002.

Superconformal Film Growth, Gordon Research Conference on Electrodeposition, New London, NH, August 13, 2002.

Superconformal Film Growth, Short Course, IEEE International Interconnect Technology Conference, Burlingame, CA, June 2, 2002.

Superconformal Electrodeposition of Copper, Surface Science and Thin-Film Growth in Electrolytes, MRS Meeting, Boston, MA, November 2001.

Superconformal Electrodeposition of Copper in 500-90 nm Features, Shipley, Inc., Marlborough, MA, November 30, 2001.

Superconformal Electrodeposition of Copper, Electrochemical Deposition and Dissolution, The 52nd International Society of Electrochemistry and The 200th Meeting of the Electrochemical Society, San Francisco, CA, September 2001.

Superconformal Electrodeposition of Copper in 500-90 nm Features, Applied Materials, Inc., San Jose, CA, April 6, 2001.

Superconformal Electrodeposition of Copper in 500-90 nm Features, 221st ACS Meeting, Symposium on Thin Films: Preparation, Characterization and Application, San Diego, CA, April 2, 2001.

Superconformal Electrodeposition of Copper in 500-90 nm Features, Molecular Structure of the Solid-Liquid Interface and Its Relationship to Electrodeposition III, the 199th Meeting of the Electrochemical Society, Washington, DC, March 27, 2001.

Superconformal Electrodeposition of Copper in 500-90 nm Features, Electrochemical Processing in ULSI Fabrication and Semiconductor/Metal Deposition III, The 198th Meeting of the Electrochemical Society, Phoenix, AZ, October 23, 2000.

Electrodeposition, New Materials and Novel Methods, Department of Chemistry, Auburn University, Auburn, AL, October 19, 2000.

Electrodeposition, New Materials and Novel Methods, Department of Chemistry, University of Georgia, Athens, GA, October 18, 2000.

STM Studies of Immersed Interfaces, NIST Visiting Panel, NIST Gaithersburg, MD, May 3, 2000.

Electrodeposition of Copper, MRS Spring 2000 Tutorial Series, Cu Interconnects: What Are the Issues, San Francisco, CA, April 23, 2000.

Electrodeposition, Novel Materials and New Methods, Materials Science and Engineering Seminar, Virginia Polytechnic Institute & State University, Blacksburg, VA, October 1999.

Electrodeposition, Novel Materials and New Methods, Joint IMEC and MTM Meeting, Leuven, Belgium, September 14, 1999.

Electrodeposition, Novel Materials and New Methods, Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany, September 13, 1999.

Electrodeposition, Novel Materials and New Methods, Workshop to Develop a Research Roadmap for Atomic Scale Manufacturing, University of Virginia, Charlottesville, VA, July 29, 1999.

Electrodeposition, Novel Materials and New Methods, The Electrochemical Society, Inc., Metropolitan New York Local Section, Iselin, NJ, May 19, 1999.

Appendix C: NIST Superfilling Publications

NIST researchers have published many articles as well as three invited book chapters on the CEAC model throughout the course of their research on superconformal growth, or superfilling. The following is a reverse-chronological summary of NIST's publications related to superfilling:

- Josell, D., T.P. Moffat, and D. Wheeler. 2007. "Superfill in the Presence of Surface Diffusion." *Journal of the Electrochemical Society* 154:D208.
- Walker, M.L., L.J. Richter, and T.P. Moffat. 2007. "Potential Dependence of Competitive Adsorption of PEG/Cl⁻/(SPS/MPS) on Cu: An *In Situ* Ellipsometric Study." *Journal of the Electrochemical Society* 154:D277.
- Moffat, T.P., D. Wheeler, and D. Josell. 2007. "Superconformal Film Growth." In *Electrocrystallization in Nanotechnology*, G. Staikov and A. Milchev, eds. Weinheim, Germany: VCH-Wiley.
- Kim, S.-K., D. Josell, and T.P. Moffat. 2006. "Electrodeposition of Copper in the PEI-PEG-Cl-SPS Additive System, Reduction of Overfill Bump Formation During Cu Superfilling." *Journal of the Electrochemical Society* 153:C616.
- Moffat, T.P., D. Wheeler, S.-K. Kim, and D. Josell. 2007. "Curvature Enhanced Adsorbate Coverage Mechanism for Bottom-up Superfilling and Bump Control in Damascene Processing." *Electrochimica Acta* 53:145.
- Walker, M.L., L.J. Richter, and T.P. Moffat. 2006. "Competitive Adsorption of PEG/Cl⁻/(SPS/MPS) on Cu: An *In Situ* Ellipsometric Study." *Journal of the Electrochemical Society* 153:C557.
- Moffat, T.P., D. Wheeler, S.-K. Kim, and D. Josell. 2006. "Curvature Enhanced Adsorbate Coverage Model for Electrodeposition." *Journal of the Electrochemical Society* 153:C127.

- Josell, D., J.E. Bonevich, T.P. Moffat, T. Aaltonen, M. Ritala, and M. Leskela. 2006. "Iridium Barriers for Direct Copper Electrodeposition in Damascene Processing." *Electrochemical & Solid State Letters* 9:C48.
- Josell, D., C. Witt, and T. P. Moffat. 2006. "Osmium Barriers for Direct Copper Electrodeposition in Damascene Processing." *Electrochemical & Solid State Letters* 9:C41.
- Moffat, T.P., and D. Josell. 2005. "Seedless Superfilling: Opportunities and Challenges." *Semiconductor Fabtech* 27th Edition 133, Henley Media Group.
- Walker, M., L. Richter, D. Josell, and T.P. Moffat. 2006. "An In Situ Ellipsometric Study of the Cl—Induced Adsorption of PEG on Ru and Underpotential Deposited Cu on Ru." *Journal of the Electrochemical Society* 153:C235.
- Moffat, T.P., M. Walker, P.J., Chen, J.E. Bonevich, W.F. Egelhoff, L. Richter, D. Josell, C. Witt, T. Aaltonen, M. Ritala, and M. Leskela. 2006. "Electrodeposition of Cu on Ru Barrier Layers for Damascene Processing." *Journal of the Electrochemical Society* 153:C37.
- Josell, D., D. Wheeler, and T.P. Moffat. 2006. "Gold Superfill in Sub-Micrometer Trenches: Experiment and Prediction." *Journal of the Electrochemical Society* 153:C11.
- Walker, M.L., L.J. Richter, and T.P. Moffat. 2005. "In-Situ Ellipsometric Study of PEG/Cl Co-adsorption on Cu, Ag and Au." *Journal of the Electrochemical Society* 152:C403.
- Josell, D., C.R. Beauchamp, D.R. Kelley, C.A. Witt, and T.P. Moffat. 2005. "Gold Superfill in Sub-Micrometer Trenches." *Electrochemical and Solid-State Letters* 8:C54.
- Moffat, T.P., D. Wheeler, and D. Josell. 2005. "Superfilling and the Curvature Enhanced Accelerator Coverage Mechanism." *The Electrochemical Society Interface* Winter:46-52.
- Moffat, T.P., D. Wheeler, and D. Josell. 2005. "Quantifying Competitive Adsorption Dynamics in Superfilling Electrolytes." In *Electrochemical Processes in ULSI and MEMS*, H. Deligianni, S.T. Mayer, T.P. Moffat, and G.R. Stafford, eds. The Electrochemical Society, pg. 23.
- Josell, D., C. Burkhard, D. Kelley, Y.-W. Cheng, R.R. Keller, J.E. Bonevich, Y. Li, B.C. Baker, C.A. Witt, and T.P. Moffat. 2004. "Electrical Properties of Superfilled Sub-100 nm Silver Metallizations." *Journal of Applied Physiology* 96:759.
- Wheeler, D., T.P. Moffat, G. B. McFadden, S. Coriell, and D. Josell. 2004. "A New Mechanism for Surface Stabilization by Adsorbed Catalyst." *Journal of the Electrochemical Society* 151:C538.

- Moffat, T.P., D. Wheeler, M. Edelstein, and D. Josell. 2005. "Superconformal Film Growth: Mechanism and Quantification." *IBM Journal of Research and Development* 49:19.
- Moffat, T.P., D. Wheeler, and D. Josell. 2004. "Electrodeposition of Copper in the SPS-PEG-Cl Additive System: I. Kinetic Measurements: Influence of SPS." *Journal of the Electrochemical Society* 151:C262.
- Josell, D., T.P. Moffat, and D. Wheeler. 2004. "An Exact Algebraic Solution for the Incubation Period of Superfill." *Journal of the Electrochemical Society* 151:C19.
- Josell, D., D. Wheeler, C. Witt, and T.P. Moffat. 2003. "Seedless Superfill: Copper Electrodeposition in Trenches with Ruthenium Barriers." *Electrochemical and Solid-State Letters* 6:C143.
- McFadden, G.B., S.R. Coriell, T.P. Moffat, D. Josell, D. Wheeler, J. Mallett, and W. Schwarzacher. 2003. "A Mechanism for Brightening: A Stability Analysis of the Curvature Enhanced Accelerator Coverage Model." *Journal of the Electrochemical Society* 150:C591.
- Baker, B.C., C. Witt, D. Wheeler, D. Josell, and T.P. Moffat. 2003. "Superconformal Silver Deposition Using KSeCN Derivatized Substrates." *Electrochemical and Solid-State Letters* 6(5):C67-C69.
- Moffat, T.P., B. Baker, D. Wheeler, and D. Josell. 2003. "Accelerator Aging Effects During Copper Electrodeposition." *Electrochemical and Solid-State Letters* 6(4):C59.
- Wheeler, D., D. Josell, and T.P. Moffat. 2003. "Modeling Superconformal Electrodeposition Using the Level Set Method." *Journal of the Electrochemical Society* 150:C302.
- Moffat, T.P., D. Wheeler, C. Witt, and D. Josell. 2002. "Superconformal Electrodeposition using Derivatized Substrates." *Electrochemical and Solid-State Letters* 5:C110-C112.
- Pyo, S.G., S. Kim, D. Wheeler, T.P. Moffat, and D. Josell. 2003. "Superconformal Deposition by Iodine-Catalyzed Chemical Vapor Deposition." *Journal of Applied Physics* 93:1257.
- Josell, D., S. Kim, D. Wheeler, T.P. Moffat, and S.G. Pyo. 2003. "Superconformal Deposition by Iodine-Catalyzed Chemical Vapor Deposition." *Journal of the Electrochemical Society* 150:C368.
- Baker, B.C., M. Freeman, B. Melnick, D. Wheeler, D. Josell, and T.P. Moffat. 2003. "Superconformal Electrodeposition of Silver from a $KAg(CN)_2$ -KCN-KSeCN Electrolyte." *Journal of the Electrochemical Society* 150:C61.

- Josell, D., B. Baker, C. Witt, D. Wheeler, and T.P. Moffat. 2002. "Via Filling by Electrodeposition: Superconformal Silver and Copper and Conformal Nickel." *Journal of the Electrochemical Society* 149:C637.
- Moffat, T.P., B. Baker, D. Wheeler, J.E. Bonevich, M. Edelstein, D.R. Kelly, L. Gan, G.R. Stafford, P.J. Chen, W.F. Egelhoff, and D. Josell. 2002. "Superconformal Electrodeposition of Silver in Submicrometer Features." *Journal of the Electrochemical Society* 149:C423.
- Josell, D., D. Wheeler, and T.P. Moffat. 2002. "Superconformal Electrodeposition in Vias." *Electrochemical and Solid-State Letters* 5(4):C49.
- Josell, D., D. Wheeler, and T.P. Moffat. 2002. "Superconformal Deposition by Surfactant-Catalyzed Chemical Vapor Deposition." *Electrochemical and Solid-State Letters* 5(3):C44.
- Josell, D., D. Wheeler, W.H. Huber, J.E. Bonevich, and T.P. Moffat. 2001. "A Simple Equation for Predicting Superconformal Electrodeposition." *Journal of the Electrochemical Society* 148:C767-C773.
- Josell, D., D. Wheeler, W.H. Huber, and T.P. Moffat. 2001. "Superconformal Electrodeposition in Submicron Features." *Physical Review Letters* 87 (1):016102.
- Moffat, T.P., D. Wheeler, W.H. Huber, and D. Josell. 2001. "Superconformal Electrodeposition of Copper." *Electrochemical and Solid-State Letters* 4(4):C26-C29.
- Moffat, T.P., J.E. Bonevich, W.H. Huber, A. Stanishevsky, D.R. Kelly, G.R. Stafford, and D. Josell. 2000. "Superconformal Electrodeposition of Copper in 500-90 nm Features." *Journal of the Electrochemical Society* 147:4524.

Appendix D: Interview Guide

The Impact of NIST's Superfilling Research

Interview Instrument

Thank you for your participation in this brief but important survey intended to collect information on the impact of National Institute of Standards and Technology's (NIST's) research on superfilling techniques for the semiconductor industry. RTI International will use the results of this survey as part of a research study commissioned by NIST. This study will provide an economic impact assessment of the value of NIST's research on superfilling in support of the U.S. semiconductor supply chain.

Nondisclosure policy

RTI has a well-established practice of dealing with confidential information as part of numerous projects. Any information obtained through these surveys will be used solely in aggregate with other information garnered from other respondents. In no instance will specific individuals or organizations be identified by name in any reports or as part of information that is released publicly or to the National Institute of Standards and Technology based on our discussions.

PART I: GENERAL INFORMATION

1. Is your parent company based in the U.S.?
 Yes
 No

2. Is the facility where you personally work located in the U.S.?
 Yes
 No

3. What is your title? _____

4. What semiconductor supply chain group do you represent? *[NOTE: If you work for a company that has activities in more than one area of the industry supply chain, please select only the group with which you are most knowledgeable. Then, please forward this survey link to an appropriate person for each of the other areas and ask them to fill out a separate questionnaire for that activity.]*
 Integrated circuit designer
 Chemical/material supplier
 Equipment supplier
 Software supplier
 Front-end processing (wafer fabrication)
 Back-end processing (packaging, assembly, and test)
 Other (_____)

5. What main products does your company produce within the group indicated in Question 4 that relate to copper superfilling?

6. Approximately, how many employees currently work at your company? _____

7. Estimated revenues:
 - a. What were the approximate gross sales of your company in the most recent fiscal year? _____

 - b. Approximately what percentage of these sales is attributable to the *group* that conducts superfill research? (If you are responding for the entire organization, enter 100%.) _____

 - c. Approximately what percentage of these sales (using the answer to Question 7b as a reference point) is related to sales of semiconductor products or products to the semiconductor industry? _____

PART 2: USE OF NIST SUPERFILL CEAC MODEL AND RELATED RESEARCH FINDINGS

1. Are you aware of NIST's Curvature Enhanced Accelerator Coverage (CEAC) model that aids in predicting superfilling characteristics?
 - Yes
 - No
 - a. If so, do you use NIST's CEAC model?
 - Yes
 - No
 - b. If so, when did you first start using NIST's CEAC model?

 - c. If so, how do you use NIST's CEAC model?

2. How did you hear about NIST's CEAC model? (CHECK all that apply)
 - Moffat et al. (2001)¹
 - Josell, Wheeler, Huber, and Moffat (2001)²
 - Wheeler et al. (2003)³
 - Presentation(s) (Please specify: _____)
 - Other (Please specify: _____)

¹ Moffat, T.P., D. Wheeler, W.H. Huber, and D. Josell. 2001. "Superconformal Electrodeposition of Copper." *Electrochemical and Solid-State Letters* 4:C26-C29.

² Josell, D., D. Wheeler, W.H. Huber, and T.P. Moffat. 2001. "Superconformal Electrodeposition in Submicron Features." *Physical Review Letters* 87:016102-1-4.

³ Wheeler, D., D. Josell, and T.P. Moffat. 2003. "Modeling Superconformal Electrodeposition Using the Level Set Method." *Journal of the Electrochemical Society* 150:C302.

3. Are you aware of the following technical findings related to superfilling and NIST's CEAC? (YES or NO for each)
- a. Link discovered between hysteresis and bottom-up filling of trenches during copper deposition (First identified in Moffat et al. [2000]⁴)
 Yes
 No
 - b. CEAC equations shown to help drastically increase the evaluation of processing parameters (First identified in Josell, Wheeler, Huber, Bonevich, and Moffat [2001]⁵)
 Yes
 No
 - c. Expanded CEAC model shown to predict the effects of changes in geometry (First identified in Josell, Wheeler, and Moffat [2002]⁶ and Josell et al. [2002]⁷).
 Yes
 No
4. During what processes have you used the CEAC model? (CHECK all that apply.)
- R&D
 - Adoption of superfill process
 - Production of ICs
 - Other (Please specify: _____)

⁴ Moffat, T.P., J.E. Bonevich, W.H. Huber, A. Stanishevsky, D.R. Kelly, G.R. Stafford, and D. Josell. 2000. "Superconformal Electrodeposition of Copper in 500-90 nm Features." *Journal of the Electrochemical Society* 147:4524-4535.

⁵ Josell, D., D. Wheeler, W.H. Huber, J.E. Bonevich, and T.P. Moffat. 2001. "A Simple Equation for Predicting Superconformal Electrodeposition in Submicrometer Trenches." *Journal of the Electrochemical Society* 148:C767-C773.

⁶ Josell, D., D. Wheeler, and T.P. Moffat. 2002. "Superconformal Electrodeposition in Vias." *Electrochemical and Solid-State Letters* 5:C49.

⁷ Josell, D., B. Baker, C. Witt, D. Wheeler, and T.P. Moffat. 2002. "Via Filling by Electrodeposition: Superconformal Silver and Copper and Conformal Nickel." *Journal of the Electrochemical Society* 149:C637.

5. What benefits did you observe from using NIST's CEAC model and associated findings? (That is, how did costs for R&D, the adoption of superfilling process, and production costs differ based on using NIST's model? Table D-1 provides example descriptions and likely beneficiaries.)

- R&D cost savings
- Superfill process cost savings
- Production cost savings

Table D-1. Example Descriptions and Likely Beneficiaries

Benefit Description	Benefit Type	Primary Beneficiary(ies)
More rapid (less costly) screening of electrolyte systems—through experimental fill studies—because of quantitative prediction of electrolytes' properties (e.g., efficacy)	R&D cost savings	<ul style="list-style-type: none"> • Chemical/material suppliers • Equipment suppliers • Device manufacturers
Improved processing through predictive understanding of superfilling mechanism, including incubation period, bottom-up filling, and overfill bump formation	Adoption cost savings Production cost savings	<ul style="list-style-type: none"> • Equipment suppliers • Device manufacturers
Extrapolation of existing results to more advanced (e.g., smaller) dimensions prior even to the availability of industrial patterned wafers with such filling geometries	Production cost savings	<ul style="list-style-type: none"> • Device manufacturers

6. Please identify and describe any costs your firm incurred to adopt NIST's research findings as part of your research and/or production processes:

- a. Training: _____
- b. New equipment costs: _____
- c. Installation costs: _____
- d. Downtime: _____
- e. Other (Please specify): _____

7. What would you have done without NIST's model? _____

a. How would you have conducted R&D? _____

b. How would your adoption of superfilling been different? _____

c. How would your use of superfilling in production been different? _____

Appendix E: Patents Citing NIST Superfilling Publications

NIST provided information on patents issues and patent applications that have, to date, cited its research in superfilling:

Patents Issued:

7341946—Novellus
7338908—Novellus
7291253—ECI Technology
7289933—Synopsys
7247563—Uri Cohen, Palo Alto
7150820—Semitool
6951599—Applied Materials
6869515—Uri Cohen, Palo Alto
6815349—Novellus
6713122—Novellus
6664122—Novellus
7124120—Technic
7335288—Novellus
7338908—Novellus

Patent Applications:

US2005/0247577—ECI Technology
US2007/0166995—IBM
US2007/0222066—IBM
US2007/0118320—Silicon Valley Patent Group
US2004/0055888—Technic

US2005/0067297—Rockwell

US2003/0029726—Applied Materials

US2007/0145507—Contact Layer for Thin Film Solar ZCells, Basol
with Solopower

US2003/0029726—Applied Materials

US2008/0099340—Tokyo, Ru oxide removal