



INTERNATIONAL  
TECHNOLOGY ROADMAP  
FOR  
SEMICONDUCTORS 2.0

2015 EDITION

EMERGING RESEARCH MATERIALS

THE ITRS IS DEvised AND INTENDED FOR TECHNOLOGY ASSESSMENT ONLY AND IS WITHOUT REGARD TO ANY COMMERCIAL CONSIDERATIONS PERTAINING TO INDIVIDUAL PRODUCTS OR EQUIPMENT.

## Table of Contents

1.	Mission and Scope .....	4
2.	Difficult Challenges .....	6
3.	Introduction and Justification .....	10
4.	Beyond CMOS Emerging Research Device Materials .....	11
5.	More Moore	
5.1.	Lithography Materials .....	12
5.2.	Emerging Front End Processes and Process Integration, Devices, and Structures' Material Challenges and Options .....	17
5.3.	Interconnects .....	18
6.	Heterogeneous Component Materials.....	18
7.	Heterogeneous Integration Assembly and Package Materials .....	19
8.	Environment, Safety, and Health .....	19
9.	Metrology .....	19
10.	Modeling and Simulation .....	22
11.	Outside System Connectivity.....	28
12.	Potentially Disruptive Convergent Application Opportunities for the Next Generation of Emerging Research Materials .....	28
13.	Transitioned Materials.....	30
14.	References .....	30

## List of Figures

Figure ERM1	Manufacturing start-up trends in information processing.....	5
Figure ERM2	Schematic summary of the collaborative ERM material and process identification, monitoring, assessment, and transition cycle.....	10
Figure ERM3	Schematic matrix of ERM Interactions with Focus Teams and ITWGs.....	11
Figure ERM4	Demonstrated 5nm half pitch using 193nm self-aligned octuple patterning. ....	12
Figure ERM5	SADP process combined with EUV lithography prints 9nm half pitch. ....	13
Figure ERM6	Adapted with permission from Ref. 2. ....	15
Figure ERM7	a) Illustration selective growth, b) Experimental demonstration .....	16
Figure ERM8	Device Material Modeling and Simulation Challenges and Needs .....	22
Figure ERM9	Modeling from Molecules to Circuits.....	24
Figure ERM10	Multiscale Modeling .....	27
Figure ERM11	Nature inspired monolithically integrated functionality.....	29

## List of Tables

Table ERM1	Near-term transitional and longer-term ERM Difficult Challenges.....	6
Table ERM2	An initial straw set of emerging research materials needs for convergent application opportunities with adjacent market sectors.....	8
Table ERM3C	Top four Beyond CMOS related ERM priorities.....	12
Table ERM4A	Patterning identified ERM challenges, courtesy of ERD-Japan.....	17
Table ERM5A	Continuing FEP/PIDS related ERM doping challenges .....	18
Table ERM6	ERM Interconnect Materials: A. Continuing Challenges and B. Top Four Strategic ERM Priorities.....	18
Table ERM7	ERM Priorities: Heterogeneous Component Materials.....	19
Table ERM8	ERM Priorities: Heterogeneous Integration/Assembly & Packaging .....	19
Table ERM9	ERM Insertion Matrix and Priorities: Environment, Safety and Health.....	19
Table ERM10C	Prioritized set of Metrology ERM Challenges and Needs.....	21
Table ERM11B	A prioritized list of ERM related difficult modeling and simulation challenges...	27
Table ERM11C	Metrology Material Modeling and Simulation Challenges and Needs.....	28
Table ERM12	Prioritized Outside System Connectivity related ERM needs.....	28
Table ERM13	Summary of potentially disruptive Emerging Research Materials application opportunities.....	30
Table ERM14	Emerging Research Materials Transition Table.....	30

# **EMERGING RESEARCH MATERIALS (ERM)**

## **1. MISSION AND SCOPE**

**Mission Statement:** The ERM mission is to identify, monitor, and assess research materials and processes that:

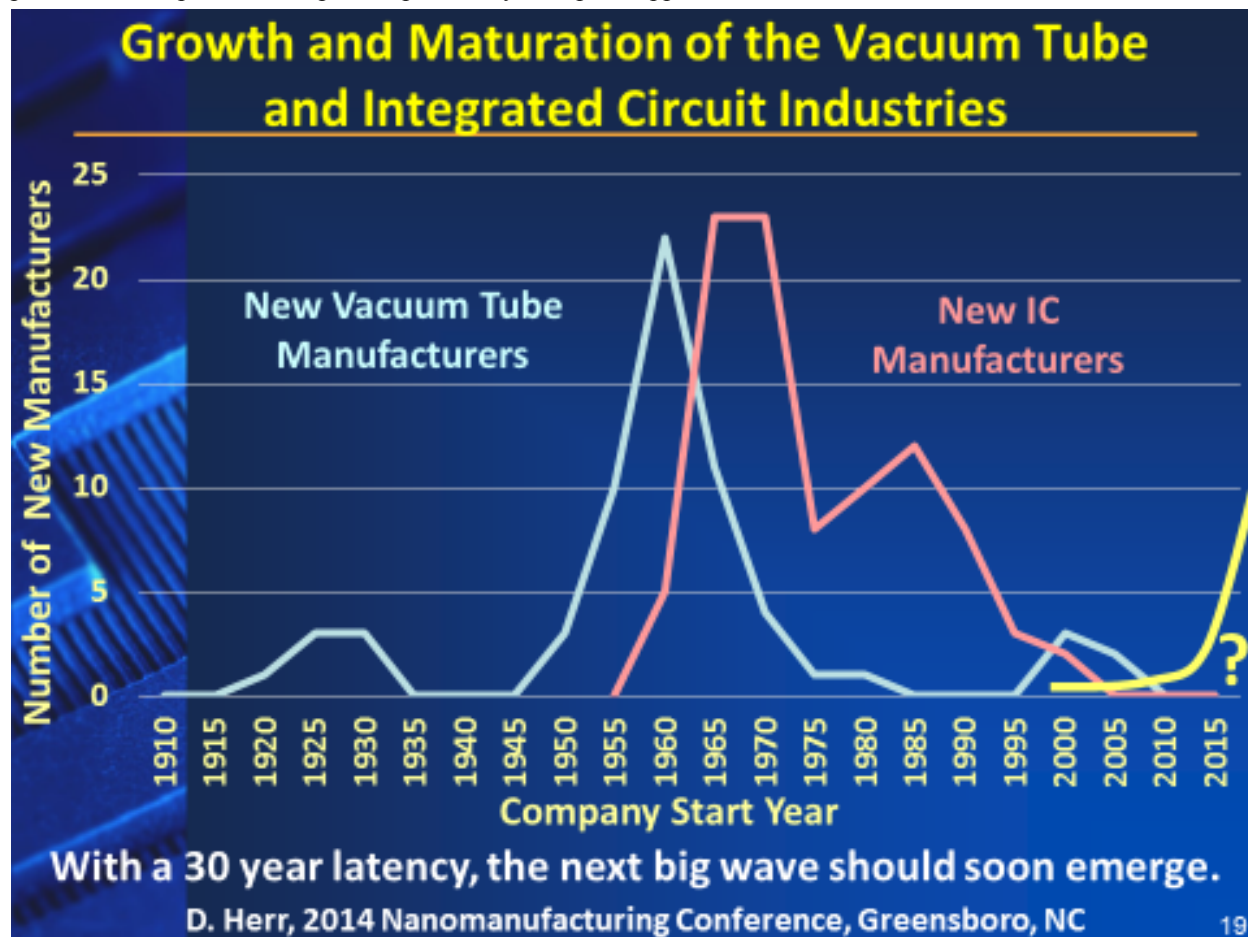
1. Have the potential to resolve identified strategic difficult challenges for International Technology Working Groups (ITWGs) and Focus Teams (FT), or
2. Enable: a) breakthrough advances in monolithically integrated functional density or b) high volume fabrication of potentially disruptive Internet-of-Things (IoT) technologies.

For mission objective #1, the ERM team strives to build consensus with relevant ITRS stakeholders to facilitate the transition of promising strategic research grade materials and processes into relevant ITWGs and FTs. Conversely, the ERM team archives less promising and more tactical materials and processes for future application opportunities. To achieve mission objective #2, the ERM team leverages and augments the existing ITRS expertise with experts from relevant market sectors, which may include new stakeholder communities, e.g. medical diagnostics, energy, aerospace, etc. The ultimate goal is to provide timely guidance on emerging material and process performance, cost, reliability, and sustainability options that will drive breakthrough advances in future manufacturing technology.

**Scope Statement:** The ERM team scope covers research phase materials and processes that exhibit potential to: 1) Address strategic difficult challenges for ITRS Technology Working Groups (ITWG) and Focus Teams (FT) having insertion horizons  $\geq 8$  years, and/or 2) Enable novel, breakthrough and potentially disruptive Internet of Things (IoT) opportunities. It emphasizes emerging material properties, synthetic methods, metrology, needs gaps and requirements, and modeling required to support strategic:

1. ***Scaled technology materials needs***, i.e. More Moore (MM), and Beyond CMOS (BC). The More Moore topics currently cover Emerging Research Devices (ERD), Lithography (LIT), Front-End Processes (FEP).
2. ***Heterogeneous Components and Integration needs***, i.e. Heterogeneous Components (HC), Heterogeneous Integration (HI), and Outside System Connectivity (OSC), and related Modeling and Simulation (M&S), Metrology (MET); Environment, Safety, and Health (ESH); and Factory Integration (FI) needs. The new Heterogeneous Integration Focus Team currently also includes System-in-Package (SiP), Interconnects (IC), and Assembly & Packaging (A&P).
3. ***Potentially disruptive material and process opportunities***, e.g. Quantum materials systems; Flexible electronics; Deterministic, multi-functional, and biomimetic materials and processes; and high impact application areas, e.g. Energy, Environment, Agriculture, Health, Medical, etc. A key strategic goal is to cultivate novel functional research grade materials that enable potentially disruptive trans-disciplinary advances in monolithically integrated complex functional density, i.e. Functional scaling.

**Background and Justification:** Figure ERM1 shows the number of vacuum tube and semiconductor start-ups by year. It also suggests that pressure is growing for the next disruptive wave of information processing technology. While ERM continues to support the evolutionary, and semiconductor centric needs of the traditional ITRS 2.0 communities, emerging architectures could benefit from new device functionality, which may require new materials and new physical mechanisms. New waves of emerging materials technologies, which may be in the ‘ugly duckling’ phase of development that represent potentially disruptive opportunities<sup>1</sup>.



**Figure ERM1.** Manufacturing start-up trends in information processing

Since 2006, the ERM team has worked closely with other ITWGs to identify, monitor, and assess emerging materials and process technologies. As ITRS 2.0 takes shape, ERM will adapt and expand its stakeholder base to engage with several Focus Teams and other emerging relevant stakeholder communities in support of the new ITRS 2.0 vision and goal set.

The ITRS 2.0 seeks a framework for managing the convergence of scaled information processing and storage, i.e. More Moore (MM) and Beyond CMOS (BC), with the next emerging era of monolithically integrated systems that achieve enhanced overall functional density, i.e. More-than-Moore (MtM). The term ‘More than Moore’, introduced in the 2005 ITRS edition, reflects the emergence of non-scaled heterogeneous integration as a key factor for driving non-digital functionalities into new generations of smart systems. The ‘More than Moore White Paper’<sup>2</sup>, released in 2010, provided an initial outline of a methodology for the MtM road-mapping process. The MtM domain requires a highly interdisciplinary set of expertise, e.g. electrical and mechanical engineering; as well as materials, biological, medical, energy, aerospace, transportation, communication, and sustainability sciences. The trend towards the convergence of monolithically integrated functional diversification with miniaturization manifests as increasing complexity in the road-mapping process. Recent ITRS editions reflect this growing complexity, with an increasing number of projected roadmap parameters and requirements associated with new functionalities<sup>3</sup>.

## 2. DIFFICULT CHALLENGES

**Selected Difficult Challenges/Show Stoppers and Potentially Disruptive Options:** Each ITWG and Focus Team has unique needs that must be addressed to meet future roadmap requirements, and realize breakthrough opportunities for enabling potentially disruptive technologies. Table ERM1 summarizes an initial set of some transitional and potentially disruptive Difficult Challenges.

<i>Difficult Challenges 2015-2022</i>	<i>Summary of Transitional Issues</i>
<i>Achieving desired properties in integrated structures</i>	<p>Identify integrated high k dielectrics with EOT &lt;0.5nm and low leakage</p> <p>Identify integrated contact structures that have ultralow contact resistivity</p> <p>Achieving high hole mobility in III-V materials in FET structures</p> <p>Achieving high electron mobility in Ge with low contact resistivity in FET structures</p> <p>Achieving a bandgap in graphene in FET structures</p> <p>Multiferroic with Curie temperature &gt;400K and high remnant magnetization to &gt;400K</p> <p>Ferromagnetic semiconductor with Curie temperature &gt;400K</p> <p>Synthesis of CNTs with tight distribution of bandgap and mobility</p> <p>Electrical control of the electron correlation, ex. Mott transition, Spin dynamics</p> <p>Simultaneously achieve package polymer CTE, modulus, electrical, thermal properties, with moisture and ion diffusion barriers</p> <p>Thermal interface materials with low interface thermal resistance and high thermal conductivity with desired electrical and mechanical properties.</p> <p>Nanosolders compatible with &lt;200C assembly, multiple reflows, high strength, and high electromigration resistance</p> <p>NanoInks that can be printed as die attach adhesives with required electrical, mechanical, thermal, and reliability properties.</p> <p>NanoInks that can be printed as conductors, via hole fillers, solders, or die attach adhesives with required electrical, mechanical, thermal, and reliability properties.</p>
<i>Characterize and control coupled properties of embedded materials and their interfaces</i>	<p>High mobility transition metal dichalcogenides TMD with unpinned Fermi level and low resistance ohmic contacts</p> <p>High electron mobility in Ge with unpinned Fermi level and low resistance ohmic contacts</p> <p>High mobility in nanowires with unpinned Fermi level</p> <p>Graphene with a bandgap, high mobility, and unpinned Fermi level at dielectric interfaces</p> <p>Complex metal oxides with unpinned Fermi levels</p> <p>Nanoscale observation of the magnetic domain structure, for example, the domain in STT-RAM under the magnetic field, i.e., the dynamic operation</p> <p>Characterization of electrical properties of molecule / metal contact interfaces (i.e. Pentacene/Au)</p> <p>Characterization of electrical properties of embedded nano contact interfaces (i.e. CNT/Metal )</p> <p>CNTs with low resistance contacts on both ends</p> <p>Characterization for density of dislocations and anti-phase boundary generating interface between Ge/III-V channel materials and Si</p>
<i>Identifying manufacturable methodologies to enable deterministic fabrication with required property control</i>	<p>Dopant placement and activation i.e. deterministic doping with desired number at precise location for V<sub>th</sub> control and S/D formation in Si as well as alternate materials</p> <p>HVM compatible methods to place dopants in predetermined positions with minimal damage to the semiconductor</p> <p>Manufacturing and purification methodologies of CNT to achieve required purity levels (pure semiconductor with bandgap)</p> <p>Identify DSA process simplification methodologies that can achieve required overlay requirements</p> <p>Wafer scale growth of high quality graphene with desired process conditions (ex. Low temperature growth on metal or insulator)</p> <p>Controlling edge-termination / molecular absorption to graphene to achieve required bandgap</p> <p>Synthesis or assembly of CNTs in predefined locations and directions with controlled diameters, chirality and site-density</p> <p>III-V: Correlation between antiphase domains and electrical properties</p>
<i>Ability to control defects in material processing</i>	<p>Methods to reduce directed self assembly based defects to &lt;0.01cm<sup>-2</sup> for litho extension</p> <p>Control defects in carbon nanotubes</p> <p>Control defects in growth and processing of graphene</p> <p>Control concentration and locations of cation and anion defects in complex metal oxides</p> <p>Control precipitation in ferromagnetic semiconductors</p> <p>Characterization for density of dislocations and anti-phase boundary generating interface between Ge/III-V channel materials and Si</p>
<i>Control of Self-assembly processes to achieve desired properties reproducibly</i>	<p>DSA for Litho Extension: Simultaneously achieve required feature sizes in predetermined arrays with low anneal time, low defect density</p> <p>DSA for Litho Extension: Efficient CAD models to enable translating design features to guide structures on photomasks.</p>

	<p>DSA for Litho Extension: Registration of self-assembled patterning materials in desired locations with control of geometry, conformation, interface roughness, and defects</p> <p>DSA for Litho Extension: Achieve realistic device pattern with reduced pattern roughness and defects</p> <p>Demonstrate self assembly's ability to deterministically control locations of dopants conformally on 3D structures</p>
<b>Difficult Challenges 2023-2030</b>	<b>Summary of Issues</b>
<i>Electric field control of the electrochemical reaction in a nanoscaled device and at an interface</i>	<p>Complex Oxides: Control of oxygen vacancy formation at metal interfaces and interactions of electrodes with oxygen and vacancies</p> <p>Switching mechanism of atomic switch: Improvements in switching speed, cyclic endurance, uniformity of the switching bias voltage and resistances both for the on-state and the off-state.</p> <p>Nano-Carbon / metal functional junction, such as new switch, by using electrochemical reactions</p> <p>Molecular device fabrication with precise control using electrochemical reactions</p>
<i>Metrology to characterize structure and properties of materials at the nanometer scale</i>	<p>Development of the method to evaluate the validity of the measurement result for each ERM</p> <p>Electrical and thermal properties of each carbon nanotube</p> <p>Nanowire characterization of mobility, carrier density, interface states, and dielectric fixed charge effects</p> <p>Graphene and TMD mobility and carrier concentration</p> <p>Complex metal oxide characterization of carrier density, dielectric and magnetic properties</p> <p>Spin materials: characterization of spin, magnetic and electrical properties and correlation to nanostructure</p> <p>Characterization of electrical properties of embedded nano-contact interfaces (ex. CNT/Metal )</p> <p>Evaluating material properties in realistic device structures</p> <p>Nanoscale observation of the magnetic domain structure, for example, the domain in STT-RAM under the magnetic field, i.e., the dynamic operation</p>
<i>Metrology to characterize defects at the nanometer scale with atomic resolution</i>	<p>CNT vacancy and interstitial ordering around dopants</p> <p>Nanowires: Characterization of vacancies, interstitials and dopants within the NW and at interfaces to dielectrics</p> <p>Graphene: Characterization of edge defects, vacancies and interstitials within the material and at interfaces</p> <p>Metal nanoparticles: Native oxide interface and crystal defects in the nanoparticle</p> <p>Complex Oxides: Location of oxygen vacancies and the valence state of the metal ions</p> <p>Spin materials: characterization of vacancies in spin tunnel barriers, and defects within magnetic materials and at their interfaces</p> <p>Evaluating material properties IN realistic nm scale devices</p> <p>Characterization of edge structure and termination with atomic resolution (ex. Graphene nano ribbon, TMD, etc. )</p>
<i>Accurate multiscale simulation for predictions of unit processes the resulting structure, properties and device performance.</i>	<p>Linkage between different scales in time, space, and energy bridging non-equilibrium phenomena to equilibrium phenomena</p> <p>Transferable simulation tools for many kinds of materials</p> <p>Development of platform for different simulation tools, such as TCAD and ab-initio calculations</p> <p>Nanowires: Simulation of growth and defect formation within and at interfaces</p> <p>CNTs: Simulation of growth and correlation to bandgap</p> <p>Graphene: Simulation of synthesis, edge defects, vacancies, interstitials, interfacial bonding, and substrate interactions.</p> <p>Atomistic simulation of interfaces for determining Fermi level location and resulting contact resistivity</p> <p>Nanoparticles: Simulation of growth and correlation to structure and defects</p> <p>Complex Oxides: Multiscale simulation of vacancy formation, effect on metal ion valence state and effect of the space charge layer</p> <p>Spin: Improved models for multiscale simulation of spin properties within materials and at their interfaces.</p>
<i>Fundamental thermodynamic stability and fluctuations of materials and structures</i>	<p>Geometry, conformation, and interface roughness in molecular and self-assembled structures</p> <p>Device structure-related properties, such as ferromagnetic spin and defects</p> <p>Dopant location and device variability</p>
<i>Materials and processes that enable monolithically integrated complex functionality</i>	<p>Integration on CMOS Platforms</p> <p>Integration with flexible electronics</p> <p>Biocompatible functional materials</p> <p>Robust long-term biotic-abiotic interfaces that avoid biofouling issues</p> <p>Leveraging convergent materials expertise in adjacent sectors</p>

**Table ERM1.** Near-term transitional and longer-term ERM Difficult Challenges

For the 2015 ITRS update, an initial set of strategic ERM related Difficult Challenges are summarized in Table ERM1. In 2015, the ERM team; in collaboration with ITRS ITWGs, Focus Teams continued to identify, monitor, assess, transition, and reprioritize the traditional set of research phase materials and processes that showed potential for addressing identified difficult challenges. Additionally, the ERM team began to identify enabling and potentially disruptive materials application opportunities, such as those shown in Table ERM2, appropriate for the semiconductor and ‘other relevant communities’ (ORCs). The phrase ‘other relevant communities’ (ORCs) refers to

technology experts in disciplines and market sectors that are not traditionally represented within the ITRS community. For example, these colleagues may reflect perspectives from the biomedical; imaging; energy; communication; and/or smart transportation, energy, textile, and construction device communities. In 2015, the ERM team began to cast a broad net to engage additional technology experts in non-traditional, but strategically relevant, disciplines and market sectors. Table ERM2 provides a gentle push and a starting point for conversations between ITWG, FC, and ORC colleagues on win-win convergent opportunities.

Sector Opportunity	ITWG, FT, or PDO Aligned ERM Challenges and Needs
Mobile Communication & Information	<ul style="list-style-type: none"> <li>▪ Smart nanocomposite materials with sensing and actuation functionality [HC]</li> <li>▪ Materials that enable flexible electronics [HC]</li> <li>▪ Novel concepts for self-aligned component assembly [HI]</li> <li>▪ Materials that enable multifunctional antennas [OSC]</li> </ul>
Smart Transportation and Automotive	<ul style="list-style-type: none"> <li>▪ Smart nanocomposite materials with sensing and actuation functionality [HC]</li> <li>▪ Materials that enable flexible electronics [HC]</li> <li>▪ Electronically adaptive coatings [HC]</li> </ul>
Big Data	<ul style="list-style-type: none"> <li>▪ Deterministic fabrication processes and materials [MM, BC]</li> <li>▪ Quantum Computation fabrication processes and materials [BC]</li> <li>▪ Materials that enable neurosynaptic processing [Not: Neuromorphic, i.e. weighted neural networks] [BC]</li> <li>▪ Materials and processes that enable nature inspired information acquisition, storage, retrieval and processing [PDO]</li> </ul>
Green	<ul style="list-style-type: none"> <li>▪ Materials that enable energy efficient/ high performance novel memory and logic devices [MM, BC]</li> <li>▪ High performance green materials and processes [HC]</li> <li>▪ Functional Sustainable and biocompatible materials [HC]</li> <li>▪ Concurrent ERM performance-sustainability assessment [HC]</li> <li>▪ Materials and processes and that enable integration of novel high performance green materials with CMOS and interconnects [HI]</li> <li>▪ Sustainable and biocompatible materials and processes and that enable integration of novel high performance green materials with CMOS and interconnects [PDO]</li> <li>▪ Energy efficient photonic interconnects and RF devices [OSC]</li> </ul>
Sustainable Energy	<ul style="list-style-type: none"> <li>▪ Materials that enable CMOS compatible power scavenging, distribution and components, e.g., <math>\mu</math>-batteries, capacitors, sensors and energy harvesting and storage devices [HC]</li> <li>▪ Materials that enable integrated <math>\mu</math>-fuel cells, <math>\mu</math>-batteries and power distribution on CMOS [HI]</li> <li>▪ Processes that enable the integration of novel high performance energy efficient materials with CMOS and interconnects [HI]</li> </ul>
Medical /Health	<ul style="list-style-type: none"> <li>▪ Materials that enable personalized diagnostics and monitoring devices, e.g., sensors; blood tests; lab-on-a-chip; etc. [HC]</li> <li>▪ Materials that enable robust, long term prosthetics and implantable devices [HC]</li> <li>▪ Materials and processes that enable multi-scale bio-system imaging [HC]</li> <li>▪ Ubiquitous Communication and Feedback of Biometric Data [OSC]</li> <li>▪ Adaptive Nature inspired materials and fabrication processes for medical and healthcare applications [PDO]</li> </ul>
Scaled	<ul style="list-style-type: none"> <li>▪ ESH: Efficient product lifecycle and risk management of chemicals and materials in processing and devices. [FI]</li> <li>▪ Materials and processes that enable high performance deterministic doping, 2D memory and carbon-based logic (MM)</li> <li>▪ Materials that enable STT memory; e.g., FM materials with out of plane magnetization; and FE memory options, e.g., FET, TJ; ReRAM; Mott [BC]</li> <li>▪ Materials that enable emerging logic options, such as FETs, e.g. Tunnel, Spin, BiS; Spin, e.g. Torque, MOSFET, FET, All, Contacts, Interfaces; Other, e.g. Nanomagnetic, Mott, Atomic [BC]</li> <li>▪ A&amp;P: Materials that enable breakthrough enhancements in interfacial adhesion or EMI shielding, novel interfaces for ultralow thermal contact resistance and novel spin shielding materials [HI]</li> <li>▪ Assembly of heterogeneous components with high performance electrical, thermal, and mechanical interface properties into reliable products [HI]</li> <li>▪ Materials that enable breakthrough enhancements in interconnects, e.g., DSA patterned barriers, hybrid CNT/Graphene/nanowire and spin transport local interconnects [HC]</li> <li>▪ Materials that enable high performance, compact, low power photonic sources, switches, MUX/DeMUX devices, and other optical devices. [HC]</li> </ul>

**Table ERM2.** An initial straw set of emerging research materials needs for convergent application opportunities with adjacent market sectors Note: FI  $\equiv$  Factory Integration, MM  $\equiv$  More Moore; BC  $\equiv$  Beyond CMOS, HI  $\equiv$  Heterogeneous Integration, HC  $\equiv$  Heterogeneous Components, OSC  $\equiv$  Outside System Connectivity, and PDO Potentially Disruptive Opportunities.

In 2016, the ERM team will continue to refine and prioritize the set of emerging research material and process technologies that target high priority Difficult Challenges, in collaboration with the relevant Focus Teams and ITWGs. This process will drive the ERM chapter to refocus on the most strategic difficult materials and process challenges and potential show stoppers, and to monitor and assess a corresponding set of relevant emerging material and process technologies. The ERM team also will ramp-up its work with expert colleagues in Other Relevant Communities (ORCs) to identify a few synergistic and potentially disruptive opportunities between the traditional ITRS community and colleagues in adjacent industries, along with corresponding materials needs, and difficult challenges. For example, inter-industry activities, such as the Semiconductor Research Corporation's (SRC's) 2010 Bioelectronics Roundtables (BERT) between the semiconductor and medical device communities, reached consensus on several product sectors that would leverage the semiconductor industry's low cost, high volume nanomanufacturing infrastructure and enable new generations of medical diagnostic and monitoring, prosthetic and



implantable device, and imaging capabilities. Additionally, the more recent SRC SemiSynBio workshop opened a transdisciplinary dialogue between the semiconductor and non-traditional synthetic biology communities on convergent opportunities between seemingly disparate disciplines. These conversations promise to uncover convergent win-win opportunities for the nanoelectronics and adjacent technology communities. The ERM team will continue to use the focus workshop process to clarify the state-of-the-art, understand strategic needs and challenges, and to identify, vet and assess each potential material and process opportunity.

A key ERM goal is to provide research guidance and metrics for the academic, industrial, and government research community. The relevant Focus Teams and ITWGs will help to assess the properties and performance of maturing research grade materials or processes against projected ITRS requirements. If a material or process progress to the point where industry considers it as a viable technology option and the ITRS stakeholder agrees, then the ERM team will transition it to the relevant stakeholder organization. The ERM team also identifies potential insertion horizons of promising materials and chemicals for the Environment, Safety and Health (ESH) ITWG to monitor, assess, and evaluate through their life cycle, as warranted, in future development, manufacturing, and products. Additionally, the ERM chapter will continue collaborations with the Metrology ITWG to identify materials metrology options and modeling and simulation capabilities required to accelerate progress in the identified materials and processes. Tactical materials and processes that have yet to satisfy projected research metrics or miss a targeted insertion window will be transitioned to other Working Groups, Focus Teams, or to archived status.

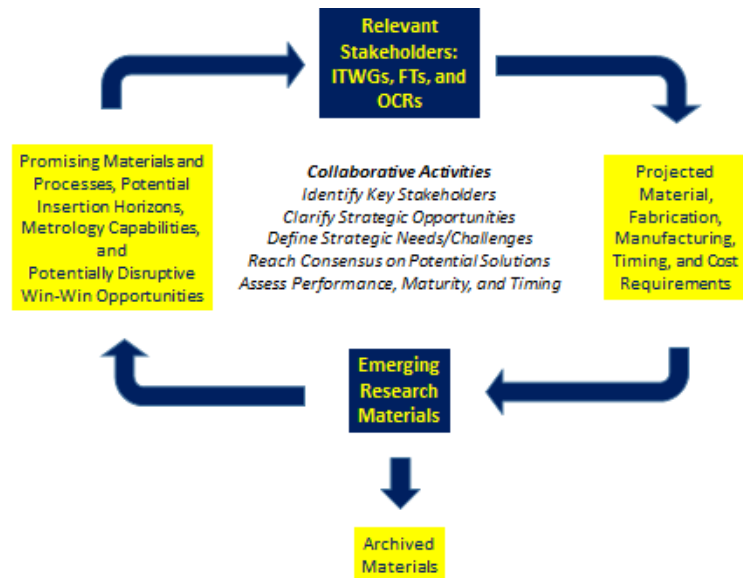
### 3. INTRODUCTION AND JUSTIFICATION

**Materials and Methodology Identification and Assessment Process:** As these new focus topics evolve, the ERM team will continue to identify, monitor, and assess new families of materials that show potential for addressing industry identified requirements and challenges. The ERM 2.0 will support a new set of drivers that enable the global industry to stay on a path of productivity and profitability, while promoting environmental health and encouraging areas of innovation for new scientists and technologists<sup>4</sup>.

Candidate ERM materials and processes exhibit unique and useful properties that may require atomic level structural, interface, defect and compositional control. In some cases, current synthetic or manufacturing technologies are not yet capable of producing such materials with the required level of control. The difficulties could be due to: 1) The inability of a research environment to produce materials with the required level of control that would express the desired properties; or 2) scaling up the synthetic and fabrication processes to satisfy commercial manufacturing requirements. In some cases, current materials growth processes effect unacceptable levels of defect formation, which drive the need for new and more robust fabrication methods. In other cases, synthetic methods exist for producing high quality materials, but these processes cannot be scaled to the higher growth rates, yields, or purity needed for insertion into viable commercial applications. While these materials may provide proof of concept and suggest a potential solution, new cost effective fabrication technologies may be required to warrant a candidate material's insertion into high volume manufacturing. For example, a prerequisite for the More than Moore road mapping process is the identification of a number of figures of merit (FOM) for specific functionalities, such as wireless communication, power generation and management, sensing and actuating. An essential feature of More-than-Moore related technologies is that candidate options depend strongly upon the application requirements, as determined by societal needs. Since the More than Moore domain represents a cross-over of the chip level and the system level technologies, the ITRS community has initiated cooperative activities with other strategic partners, such as iNEMI (International Electronics Manufacturing Initiative), to effectively address the interdependent technology/design/application requirements. Various ITWGs, including ERM, and Focus Teams are engaged in this effort to develop appropriate figures of merit that align with the new and dynamic road mapping environment. As a first pass straw proposal, the A&P team recently recommended functional density, cost, and global networking as foundational figures of merit over the ITRS 2.0's fifteen year horizon as a starting point for ITWG and FT discussions<sup>5</sup>.

The ERM team will continue to apply the same collaborative process, as in years past, for identifying and assessing materials and process performance and maturity. This process is shown schematically in Figure ERM2, below. This methodology leverages the device assessment process developed by the ERD team, more than a decade ago.

**Figure ERM2.** Schematic summary of the collaborative ERM material and process identification, monitoring, assessment, and transition cycle.



### Cross-Cutting Collaborations and Leveraged Non-Traditional Expertise:

**Metrology:** Tool sets are needed that correlate emerging research materials nanostructure, composition, and defects with the macroscopic material properties; however, current metrology tools may not necessarily be capable of correlating composition, nanostructure, and nanoscale defects with desired macroscopic properties and performance. Such non-destructive measurement capabilities may facilitate the identification of material nanostructures and issues that may cause critical problems and warrant greater focus. Furthermore, the structural or compositional metrology can examine only small volumes / regions and may not be able to unequivocally identify the most significant set of defects.

**Modeling and Simulation:** Material modeling and simulation are needed over multiple length and timescales to predict synthesis, structure, properties, and their interdependent interactions. Even in research, predictive modeling is needed to help provide a foundational understanding of the atomic scale structures that will occur as a result of specific growth conditions. Furthermore, modeling is needed to predict the effect of specific atomic level defects on material properties. Currently, researchers can simulate how a specific defect will affect local electronic properties, but expanding this to long range properties requires extrapolation and interpretation. Thus, the correlation between growth factors with observed properties remains a difficult challenge. Also, predictive capabilities are needed to assess how various growth techniques will affect the resulting nanostructures, buried local interfaces, defects, and the resulting material properties.

**Environment, Safety and Health:** The ESH properties of many promising emerging research materials have yet to be characterized or may require special care in handling. A wide range of rare earth compounds are being investigated for novel device applications; however, little is known about their potential biological interactions in compound form or after processing. Similarly, nanomaterials have properties that make them candidates for many applications, but their interactions with biological organisms are still in research phases of study. Thus, research is needed to understand the interactions of emerging research materials with biological systems.

**Interactions:** In 2015, the ERM team began to transition and archive tactical families of material candidates, with potential insertion dates through 2022, and focus its efforts on identifying, monitoring, and assessing strategic (2023-2030) emerging materials challenges, identified by the Focus Teams and the ITWGS. The current set of ITWGs with strong ERM linkages include Emerging Research Devices (ERD); Lithography (LIT); Front End Processing (FEP); Process Integration and Devices (PIDS); Interconnect (INT); Assembly and Packaging (A&P); Environment, Safety, and Health (ESH); Metrology (MET); and Modeling and Simulation (M&S). Additionally, ERM and the Design (DES) ITWG also plan to continue discussions on strategic materials and processes that enable the emergence of design for manufacturing and application driven designs with emerging lithographic/patterning materials. The ERM team also began to support the strategic emerging materials needs of six new Focus Teams (FTs), i.e. Outside System Connectivity (OSC); Heterogeneous Integration (HI); Heterogeneous Components (HC);

More Moore(MM); Beyond Moore (BM), and Factory Integration (FI). These new FTs will identify new materials attributes that will enable the high priority ITRS 2.0 needs, and potentially disruptive application drivers. The ERM ITWG also remains open to develop linkages to support the System integration (SI) team, as warranted.

Expertise Teams (Focus Teams & iTWGs)													
Focus Team or iTWG	FI	M&S	HI(A&P)	HC(MEMS)	Litho	PEP	RF/AMS	ESM (FI)	IC (HI)	Metrology	MM(PDS)	OSC	SM(EMD)
ERM	2	2	1	1	1	1	2	2	1	1	1	1	1
Interaction Priority													
LEVEL 1=ABSOLUTELY NECESSARY													
LEVEL 2= NEED OCCASIONAL SYNCHRONIZATION													
LEVEL 3= NICE TO KNOW													

**Figure ERM3.** Schematic matrix of ERM Interactions with Focus Teams and iTWGs

**The ERM 2.0 Team:** The current ERM ITWG is composed of experts from industry (chip-makers as well as their equipment and materials suppliers), government research organizations, and universities. The demographics reflect the affiliations that populate the technology domains. Since the Emerging Research Materials ITWG provides stewardship over a long-term focus area, the percentage of research participants is higher than that for suppliers. The ERM ITWG 2.0 team retains and continues to leverage the current expertise. As the new Focus Teams identify additional emerging research materials needs, the ERM 2.0 team may expand to include experts, in those areas, who can contribute to identifying, monitoring, and assessing these emerging and convergent material opportunities. The ERM team also is expanding its membership to include experts in non-traditional disciplines and market sectors to explore synergistic and potentially disruptive opportunities in adjacent spaces, such as those listed in Figure ERM3, above.

## 4. BEYOND CMOS EMERGING RESEARCH DEVICE (ERD) MATERIALS

This year’s update provides a reprioritization of the ERD’s strategic emerging materials needs, research targets, and estimates of the corresponding first potential insertion dates. The reprioritized set of continuing emerging research device materials needs are listed in Table ERM3. Table ERM3C is listed below, provides a summary of recent additions to this table, courtesy of the ERD Japan team. For additional Beyond CMOS related ERM needs see Table ERM3A and ERM3B. Additional Beyond CMOS-ERM challenges and critical materials parameters include sensors and novel materials with surface sensitivity, e.g. graphene and other 2D materials, multi-ferroic and phase transition materials, etc.

Beyond-CMOS (ERD) items	Top Beyond CMOS Emerging Research Material Needs
2D channel FET (plan to introduce in 2015 update)	2D materials: transport properties, bandgap, fabrication, ...
Novel STTRAM (plan to introduce in 2015 update)	Perpendicular magnetic anisotropy materials; materials for voltage controlled magnetic anisotropy; materials for giant spin Hall effects
Transducer-sensor pair (name undecided, plan to introduce in 2015 update)	Starting with materials for piezotronic transistor (IBM) and expand to other similar concepts
Carbon-based memory (introduced in 2013 update)	Carbon materials in various forms (graphene, CNT, a-carbon, ...) used in memory devices
FeFET memory (introduced in 2013 update)	Ferroelectric dielectrics, particularly doped HfOx

**Table ERM3C.** Top four Beyond CMOS related ERM priorities

## 5. MORE MOORE

### 5.1. PATTERNING/LITHOGRAPHY MATERIALS

Critical challenges for lithographic materials are identified and discussed. Focus is on resolving patterns of pitch sizes at

12 nm and less, mitigation of line width roughness, mitigation of edge placement error, and finally, emerging resist materials manufacturing challenges.

### 5.1.1 CRITICAL LITHOGRAPHY CHALLENGES: RESOLUTION

As Moore’s law extension continues over the next 20 years, a critical challenge emerges in terms of ultimate resolution of lithographic materials. If we use the classic Rayleigh equation to predict the ultimate way to resolve 5nm half pitch, we get some frightening prospects.

$$\text{Resolution} = (k_1 * \lambda) / \text{NA}$$

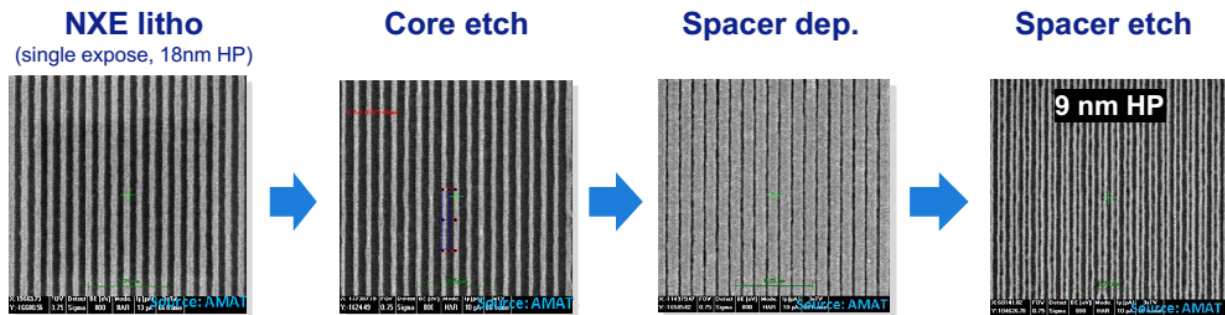
Where  $k_1$  is a dimensionless figure of merit which has been pushed as low as 0.3 in lithographic manufacturing,  $\lambda$  is the wavelength of the exposing system, and NA is the numerical aperture of the exposing system.

If we use this equation with current exposing capability and solve for  $k_1$ , with  $\lambda$  of 193nm and NA = 1.35, we get a  $k_1$  of 0.035 for resolving 5nm half pitch. So, we have to operate at a  $k_1$  factor ~9x less than ever done in lithographic manufacturing. It is astounding, however, to realize that 5nm half pitch is possible using 193nm exposure using self-aligned octuplet patterning today<sup>6</sup>, as shown in Figure ERM4! However, the cost of multiple exposures and/or deposition and etch steps and the consequent edge placement error makes this approach highly unlikely in manufacturing.

	Image	CD nm	steps
SAOP		5	> 8x

Figure ERM4. Demonstrated 5nm half pitch using 193nm self-aligned octuple patterning. [5]

Of course, it is expected that EUV lithography will have matured in 10 years or less, and as such, a much shorter  $\lambda$  of 13.5 nm will be used. The highest NA projected on the ASM-L roadmap is 0.50. Using these figures for 5nm half pitch, we get a more reasonable  $k_1$  of 0.18, which is a lot closer to 0.30. Although single patterning will not achieve the desired resolution, self-aligned double patterning (SADP) is a suitable alternative. IMEC has already demonstrated 9nm half pitch resolution with EUV SADP using a chemically amplified resists<sup>7</sup>, as shown in Figure ERM5. Continued evolutionary tool and resist development will be required to meet the 5nm target with sufficient process



window and linewidth roughness and edge placement errors.

Figure ERM5. SADP process combined with EUV lithography prints 9nm half pitch.

Berggren *et al.* have demonstrated 4nm-isolated trenches using electron beam lithography with commercial HSQ materials. However, this approach is not practical for large area dense patterning as throughput is woeful for this exposure approach, and HSQ is also a very slow resist material<sup>8</sup>.

EUV resist development has mostly centered on traditional chemically amplified (CA) resist technology. Optimization of EUV CA resists has focused on improving resist absorption, reducing the effects of out-of-band radiation, low acid diffusion and pattern collapse mitigation strategies. As features move to 5nm regime, resist absorption and pattern

collapse become very difficult to overcome. Many researchers are actively pursuing the design of metal-containing resists that have high intrinsic EUV absorption and, because of their superior etch resistance, can be processed at lower aspect ratios than CA resists. Metal-containing resists have many practical barriers to overcome, the most concerning being metal contamination of the underlying device and defectivity control.

There are other avenues to high resolution that are being explored. One exciting new approach is through directed self-assembly (DSA) which has been very actively pursued by the lithographic community. Block copolymer assemblies are known to form nanostructures with pitches approaching 5 nm. Zhang *et al.* have demonstrated sub-10 nm lines using chemoepitaxy with a high- $\chi$  organosilicon block copolymer<sup>9</sup>. However, DSA must be demonstrated to meet requirements for defectivity, roughness, and placement error, to be adopted into high volume manufacturing.

Another alternative for high resolution patterning is electron beam-induced deposition (EBID)<sup>10</sup>, a high resolution direct write lithography technique capable of writing single nanometer patterns. An electron beam is focused onto a sample in a scanning electron microscope (SEM) and reacted with a precursor gas bled into the SEM through a nozzle positioned in proximity to the substrate. The gas molecules are dissociated into a volatile part, which is pumped out of the SEM, and a nonvolatile part, which remains on the sample surface, forming a deposit. Typical precursors are W(CO)<sub>6</sub> and trimethyl (methylcyclopentadienyl)-platinum (IV) (MeCpPtMe<sub>3</sub>), which lead to tungsten and platinum deposits, respectively. At this stage of development, it is hard to imagine high throughput for such an approach, but perhaps the use of more powerful sources such as EUV might enable it.

## 5.1.2 LWR MITIGATION: MATERIALS, PROCESSES AND FUNDAMENTAL UNDERSTANDING

Line edge roughness and line width roughness (LER/LWR) have not scaled in proportion to feature size due to the stochastic nature of the lithography process and thus remains some of the biggest challenges in the sub-30-nm feature size regime.

### 5.1.2.1 LWR CHARACTERIZATION

LER/LWR in lithography are best characterized by the roughness power spectrum density (PSD), or similar measures of roughness frequency and correlation. Sun has developed a new method that combines the standard deviation and power spectral density (PSD) methods<sup>11</sup>. In this new method, the standard deviation is calculated in the frequency domain instead of the spatial domain as in the conventional method. Pattern wiggling is detected quantitatively with a wiggling factor<sup>12, 13</sup>. Other models show that post-process smoothing works best by increasing the correlation length. Increasing the correlation length is very effective at reducing high-frequency roughness that impacts within-feature variations, but is not very effective at reducing low-frequency roughness that impacts feature-to-feature variations. It seems that post-process smoothing is not a complete substitute for reducing the initial roughness of resist features<sup>14</sup>.

### 5.1.2.2 PATTERNING TECHNIQUES

Among the different next generation lithography techniques, multibeam electron beam exposure has demonstrated capability of producing low LWR 32nm/32nm L/S patterns. Exposure of biased designs in which the exposed area is reduced showed a great effectiveness to lower LWR (down to around 3.0nm)<sup>15</sup>. Fouchier found that plasma etching reduces the LER at each etching step<sup>16</sup>. The reduction is more important when starting from untreated photoresist (PR) which has the highest initial LER. However, the final LER in the Si layer remains significantly smaller when starting with cured PR, especially with PR cured by an HBr/O<sub>2</sub> plasma treatment followed by a bake at 150°C<sup>17</sup>. A break-down study with the patterning steps shows that etch, thin film deposition, and wet cleans were all process steps that positively impact LWR<sup>18</sup>. Pargon investigated the smoothing mechanisms involved in thermal treatment and showed that LWR reduction is linked to the outgassing of deprotected leaving groups present at edge surfaces of the photoresist pattern<sup>19</sup>. Thermal treatment is not as efficient as plasma treatment to reduce 193nm photoresist LWR, but the combination of thermal and plasma treatments could lead to further improvements in LWR<sup>19</sup>. Among all plasma chemistries, H<sub>2</sub> plasmas seemed

promising to decrease resist LWR over the whole spectral range, while maintaining square resist profiles<sup>20</sup>. This smoothing is mainly triggered by the synergy of H<sub>2</sub> radical and ionic species during plasma treatment<sup>21, 22</sup>.

### 5.1.2.3 PATTERNING MATERIALS

New materials development for improving LER/LWR is continues within the EUV and other areas. The key challenge for EUV resist is the simultaneous requirement of ultrahigh resolution (R), low line edge roughness (L) and high sensitivity (S) for line/ space (LS) features. New protecting groups for resist<sup>23</sup> and new photoacid generators (PAGs) having low acid diffusivity were designed. By reducing the diffusivity of the counter ions in the PAG, LWR was reduced by 60% using laser post-exposure thermal treatment (PEB)<sup>24</sup>. Both resolution and sensitivity were improved simultaneously by controlling acid diffusion length and efficiency of acid generation using novel PAG and sensitizer<sup>25, 26, 27</sup>

Among metal oxide nanoparticle type resist compositions, tin carboxylate negative tone photoresists in particular show exceptionally good LER<sup>28</sup>. Frommhold has synthesized a new resist molecule and investigated its high-resolution capability<sup>29</sup>. The material showed L/S resolution of 14 nm half-pitch (hp) and the potential to pattern 11 nm hp features. LER values as low as 3.2 nm were seen in optimized formulations, which is 3x higher than what is required<sup>29</sup>. Another strategy to improve EUV sensitivity is to include EUV sensitive units in underlayers; for example, an EUV sensitive unit formulated in a Si-hard mask underlayer strongly promoted acid generation from the PAG of an EUV photoresist<sup>30</sup>.

### 5.1.3 EDGE PLACEMENT ERROR MITIGATION

Edge placement error (EPE), the deviation in placement of the edges of features from their intended positions, has been identified as one of the largest threats to Moore's Law<sup>31,32</sup>. Multiple pathways exist for continued scaling, so-called "complementary lithography", with options including combinations of 193i with EUV, e-beam, or DSA. Multiple 193i exposures have been used to extend well beyond the single exposure limits, but as features continue to shrink, controlling EPE is becoming the biggest threat to scaling. Consider the representative logic layout in Figure

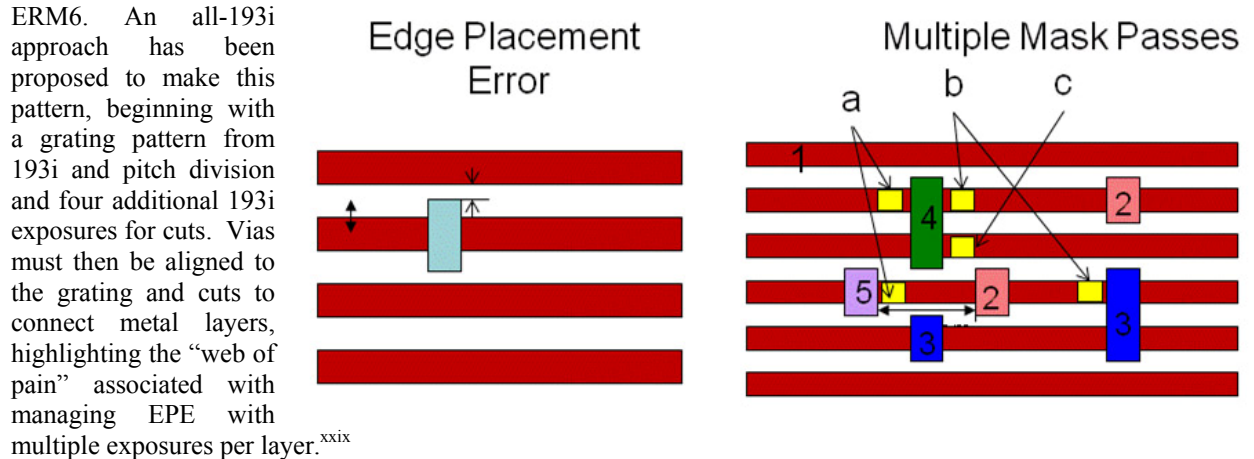
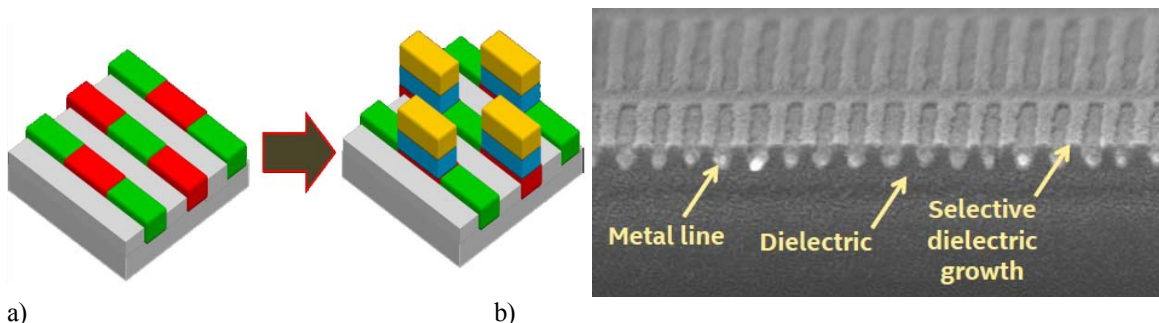


Figure ERM6. Adapted with permission from Ref. 7.

Many factors contribute to EPE, including tool overlay, CD and CDU, LER and LWR, etch bias, and variability in thin film deposition. Overlay is an obvious contributor, and continuous improvements have yielded 193i tools that can currently achieve on product overlay  $3\sigma$  as low as  $2.5\text{ nm}$ <sup>33,34</sup>. However, as total EPE budgets continue to fall, further improvements will likely be necessary to enable continued proliferation of 193i. Regardless of the technology used for imaging (193i, EUV, e-beam), photoresists must continue to deliver improved roughness and uniformity. Of particular importance is reducing low frequency line edge roughness, and several post-treatment processes have been proposed, but in general, those processes are not effective to reduce roughness at low frequencies.<sup>8</sup> One process that has shown promise for improving roughness in directed self-assembled patterning is sequential infiltration synthesis (SIS), where a resist-like material is infiltrated with a metal oxide, resulting in a hardened line, and in some cases, improved LWR<sup>35</sup>.

Another attractive option to mitigate additional overlay error inherent to multiple exposures is spacer based self-aligned double patterning<sup>36,37</sup>. These processes use photolithography to define an initial set of features that are then over-coated with a layer of spacer material. Although spin-on spacer materials and processes have been developed<sup>38,39</sup>, the processes normally utilize chemical vapor or atomic layer deposition to apply the spacers. Atomic layer deposition<sup>40</sup> is particularly attractive due to the atomic level uniformity afforded by the process. After removal of the core, the pattern density is then doubled without an additional exposure. These deposition and etch processes can be repeated several times, resulting in various pitch division schemes, even octuple patterning.<sup>vi</sup> However, every division leads to additional EPE from variations in etch and deposition.

Recently, selective growth has been proposed as an exciting patterning option with potential to mitigate EPE concerns<sup>41</sup>. This intriguing concept involves selectively growing or depositing material vertically to replicate a 2D pattern into a 3D one (Figure ERM7a). In principle, selective growth would enable placement of features in prescribed locations by utilizing the location of the features on the wafer rather than relying on machine overlay to place subsequent features. Some examples of selective growth are known and can be generally classified as either inherently selective<sup>42</sup> or selectivity mediated by a blocking layer<sup>43</sup>. For example, researchers at Intel were able to deposit dielectric on dielectric by metal passivation with a phosphonic acid (Figure ERM6b)<sup>44</sup>. These schemes have potential to improve patterning at future nodes by eliminating or mitigating many sources of EPE.



**Figure ERM7.** a) Illustration selective growth, b) Experimental demonstration (from Ref. 44).

## 5.4 MANUFACTURING CHALLENGES IN LITHOGRAPHIC MATERIALS MANUFACTURING

Profitable state of the art IC manufacturing is predicated on achieving acceptable yields, which in logic type devices generally requires maintaining a defectivity of approximately  $<0.01$  printable defects/cm<sup>2</sup>, although a somewhat higher level is tolerable in memory devices due to redundancy in the designs<sup>45</sup>. Simultaneously, leading chip designs also require trace metal ion contamination levels to be below 1 ppb<sup>46</sup> in order to achieve predictable electrical functioning. Furthermore, batch photospeed control is required to be within  $\pm 1\%$ , and critical dimension control within  $\pm 1\text{ nm}$ <sup>47</sup>. Such requirements, while technically challenging, also significantly increase the expense of the PR manufacturing and quality control. Other challenges to the economics of photoresist manufacturing include increasing product customization for critical level lithography, which results in manufacturing more products of smaller batch sizes, reducing the benefits of manufacturing scaling<sup>48</sup>. Finally, the cost of maintaining state-of-the-art immersion 193 nm phototools is expensive, and the depreciation and operational costs of EUV tools probably exceeds the ability for a resist company to possess its own, leading to licensing consortia-based EUV tools combined with locating resist manufacture in close proximity<sup>49</sup>.

Many studies have focused on the minimization of defects in PRs and in directed self-assembly materials and processes. One notable line of investigation uses *in situ* high speed photography to capture the nuances and

Technology	Critical Factor	Material	Material Challenges	Research Targets
Resist Materials	TBD	ArF resist, EUV resist, extension materials	Minimize roughness, high sensitivity, critical resolution	TBD
Resist Materials	ARF RESIST IMPROVEMENTS AND EXTENSION OPTIONS	Extension materials	Improve overlay, decrease # of multi pattern process	TBD
Resist Materials	EUV	Chemically and non-chemically amplified	Overcome RLS trade-offs	TBD
Resist Materials	NON-CA RESIST AND INORGANIC RESIST	Metal resists	Overcome RLS trade-offs	TBD
Resist Materials	HYBRID EUV APPROACHES	Organic and inorganic hybrid resists	Overcome RLS trade-offs	TBD
Directed Self Assembly for Lithography Extension	TBD	BCP, Neutral layer, Guide resist	Morphology control, minimize defectivity, placement error	TBD
Directed Self Assembly for Lithography Extension	DEFECT DENSITY	Dislocation, missing holes	Minimize defectivity, process control	TBD
Directed Self Assembly for Lithography Extension	OVERLAY CAPABILITY	TBD	DSA placement error	TBD
Directed Self Assembly for Lithography Extension	POLYMERS FOR SUB 10NM PATTERNING	High chi BCP	Vertical lamella or cylinder, etching selectivity	TBD
Directed Self Assembly for Lithography Extension	DEVELOPMENT & ETCH RESISTANCE	Wet development, dry etching	Etching selectivity	TBD
Directed Self Assembly for Lithography Extension	MATERIALS FOR PROCESS SIMPLIFICATION	DSA scheme	Hole shrink, Hole reification, pitch split	TBD
Directed Self Assembly for Lithography Extension	DESIGN TOOLS	DSA specific DFA	MASK OPC, design	TBD

previously unseen dynamic phenomena originating in coating and drying behavior developer rinsing<sup>50</sup>. In general, for litho materials, the most promising approaches to materials origin of defect reduction have been controlling the uniformity of polymer compositions and sequencing<sup>51</sup> and control of the hydrophobicity and zeta potential of surfaces to discourage redeposition of suspended organics<sup>52</sup>, commonly referred to as ‘blob defects’<sup>53</sup>. For DSA materials, there have been many studies directed at the thermodynamic origins of assembly related defects<sup>54</sup>, extinguishing kinetically trapped defects<sup>55</sup>, formulated block copolymers<sup>56</sup>, and improvements in block copolymer polymer manufacturing and solution filtration<sup>57</sup>.

Much research is also underway on filtration improvements and optimization. Key factors which impact defectivity include filtration rate, pressure drop, recirculation, and point of use filtering. Membrane choice is important to success, and many membrane material and pore size choices are available, including Teflon, polyethylene, **Table ERM4A. Patterning identified ERM challenges, courtesy of ERD-Japan.**

polypropylene, and Nylons. The best reported results are observed when multiple membrane types are used in sequence, and the sequence is customized to the particular PR formulation<sup>58</sup>. Point of use filtration has been combined with metal ion removal using embedded or layered ion exchange beads for further purity improvement<sup>59,60</sup>. Table ERM4A, above, provides some patterning related ERM challenges, courtesy of the ERD-Japan team. Additional patterning related materials challenges are summarized in Table ERM4B and ERM4C.

## 5.2. EMERGING FRONT END PROCESSES’ AND PROCESS INTEGRATION, DEVICES, AND STRUCTURES’ MATERIAL CHALLENGES AND OPTIONS

Table ERM5 provides a set of continuing FEP-PIDS related doping, ERM5A, and alternate channel, ERM5C, needs and materials challenges. Table ERM5A is listed below.

Table ERM5A. Continuing FEP/PIDS related ERM doping challenges

Additional FEP/PIDS related ERM challenges and critical materials parameters include: Gate stack, deterministic doping, selective deposition, etch material selectivity, in-situ + conformal doping, low-variability WF metals, low-resistivity contact materials



### 5.3. INTERCONNECT MATERIALS

Table ERM6 provides a set of continuing interconnect related ERM challenges and materials needs.

**Table ERM6. ERM Interconnect Materials: A. Continuing Challenges and B. Top Four Strategic ERM Priorities**

An additional Interconnect related ERM challenge includes new metals, selective deposition, air gap integration, high-k materials for MIMCAP.

### 6. HETEROGENEOUS COMPONENT MATERIALS

Key heterogeneous component ERM challenges include materials and processes that enable integration of multiple sensor types into a single package, e.g. silicon, flexible, etc.

Application	Potential Value	Process Option	Key Challenges	Target/Goal	Status
Deterministic Doping	Reduced variation in transistor performance Highest focus will be on S/D dopant lateral abruptness (Maintain high concentration of active dopants with an abrupt transition)	Single ion implant	Dopant placement < 10nm with high through-put	TBD	
		STM positioning	Dramatically higher throughput and extending to different materials and dopants		
		Block co-polymer self assembly	Long range order & smaller size <5nm	<5nm	
		Langmuir self assembly	Long range order & smaller size <5nm	<5nm	
		Hybrid approach of implanting through directed block co-polymer self-assembled structure	Long range order & smaller size <5nm	<5nm	
		Dopant electrical activation	Low thermal budget; ms-timescale energy pulses, Microwave uniformity	TBD	

Table ERM7 provides a set of top heterogeneous component material priorities for ERM.

**Table ERM7. ERM Priorities: Heterogeneous Component Materials**

### 7. HETEROGENEOUS INTEGRATION ASSEMBLY AND PACKAGING MATERIALS

The ERM and Heterogeneous Integration teams are in the process of prioritizing key heterogeneous integration and assembly & packaging ERM challenges, which include:

- New engineered materials: substrate, mold, underfill, wafer bond alloys, solder alloys
- Conductors: Nanomaterials (CNT, graphene, NWs), metals (Cu, Al, W, Ag, etc.), composites
- Dielectrics: Oxides, polymers, porous materials, composites
- Semiconductors: Elemental (Si, Ge), Compounds (III-V, II-VI, tertiary), polymers
- Critical factors: Cost, CTE differential, thermal conductivity, fracture toughness, modulus, processing temperature, interfacial adhesion, operating temperature, and breakdown field strength
- IoT/II medical device related ERM challenges and critical materials parameters:
- Chronic biotic – abiotic interface degradation and biofouling

Table ERM8 provides a set of heterogeneous integration and assembly and packaging priorities for ERM.

**Table ERM8. ERM Priorities: Heterogeneous Integration/Assembly & Packaging**

## 8. ENVIRONMENT, SAFETY, AND HEALTH

Table ERM9 includes the 2013 version of the Potential Insertion Matrix for Emerging Research Materials. In 2016, the ERM team plans to update this set of materials and potential insertion dates in collaboration with the relevant Working Groups and Focus Teams.

**Table ERM9. ERM Insertion Matrix and Priorities: Environment, Safety and Health**

An additional ESH related ERM challenge includes energetic materials and ERM based on green chemistries.

## 9. METROLOGY

Metrology is needed to characterize composition, properties, and understand structure of emerging research materials (ERM), at nanometer dimensions and below. The most difficult ERM metrology challenges would be those associated with the introduction of directed self-assembly (DSA), such as evaluating critical material properties, size and location of features, registration, and defects. Also needed are non-destructive methods for characterizing embedded materials and interfaces defects, as well as platforms that enable simultaneous measurement of complex nanoscopic properties, and modeling of probe-sample interactions.

Among the other high level ERM metrology challenges is the need to monitor and map local variation at nanoscale dimensions while providing this information across a large area, such as a 450 mm wafer. As feature dimensions start to approach those of its material’s phonon mean free path, thermal properties can diverge from their bulk or thin film forms. Thus, the Metrology Roadmap continues to emphasize the need to link modeling and simulation studies with metrology to help bridge the gap between nanoscale characterization and metrology capable of monitoring properties across a large area. This bridging effort will require valid nanoscale materials property values for use in metrology models. In addition to measurement and characterization, the environmental impact of emerging materials should be assessed at the earliest possible time. Understanding nanomaterials’ behavior in the workplace and environment is required to establish good risk assessments and material management practices.

Table ERM10 summarizes the current set of continuing and prioritized metrology related ERM challenges and needs. The prioritized list of key metrology ERM challenges, brief descriptions of the issues involved and examples are described in Table ERM10C, below.

Metrology ERM Challenge (Priority)	Difficult ERM Challenge and Strategic Material Needs
DIRECTED SELF-ASSEMBLY (DSA) (Priority 1)	For directed self-assembly (DSA) to be viable as a lithography extension or to assemble nanostructured materials in predefined locations and alignment, metrology is needed to evaluate critical material properties, the <u>size and location</u> of features, and the <u>registration</u> to previously patterned structures <sup>61,62,63</sup> . Characterization techniques are needed to evaluate neutral surfaces and the interfacial energy between the chemical surfaces and the polymers. Metrology capabilities to detect defects over large areas and under the surface are also needed. In addition, there needs to be increased focus on higher chi X materials for smaller features, and this may potentially require neutral top surfaces as well. Optical, electron and scanning probe methods <sup>64, 65</sup> have been used in DSA metrology, but new characterization techniques should leverage a combination of physical and chemical properties.
INTERFACES AND EMBEDDED NANO-STRUCTURES (Priority 2)	Emerging research materials will be integrated with other materials and will form interfaces which dominate nanostructured devices. Thus, understanding and control of the atomic structure, composition, bonding, defects, stress, and their effects on nanoscopic properties at these interfaces is critical. While some progress has been made towards nondestructive characterization of structural and electronic properties of buried interfaces, embedded contacts and other heterostructures using visible-ultraviolet internal photoemission <sup>66</sup> and scanning microwave probe methods <sup>67,68</sup> , further progress is needed. As alternate state variables are explored for Beyond CMOS, there is a need for correlated, multimodal microscopies, and modeling of probe-specimen interactions to maximize information return from nanoscale objects and interfaces.
CHARACTERIZATION AND IMAGING OF NANO-SCALE STRUCTURES AND	To enable fundamental understanding and improvement of new materials for integration into nanometer scale structures, metrology is needed to characterize the atomic structure and composition of a wide range of new complex materials, such as 2-dimensional materials such as graphene, boron nitride, meta- chalcogenides (e.g., MoS2), etc. Nondestructive in-situ measurement methods that offer real time characterization of material nanostructure, composition and orientation, while also allowing for correlation to macro

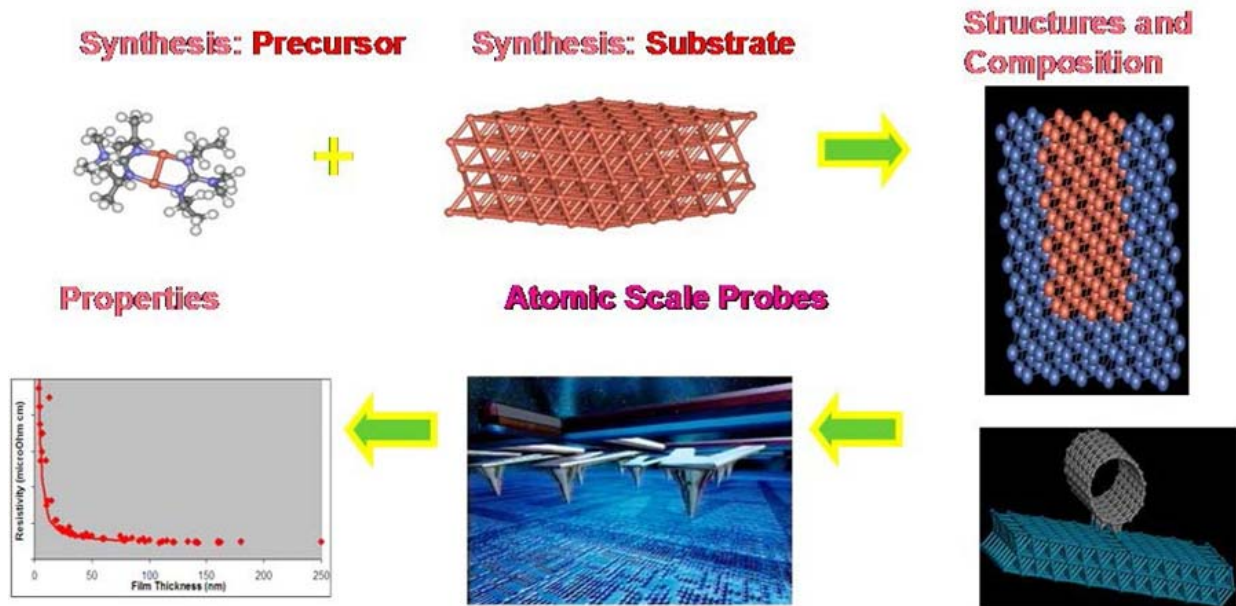
COMPOSITION (Priority 3)	properties are also needed. Research on emerging materials could benefit from further standardization <sup>69</sup> of electrical characterization methodologies to enable direct comparison of the data from various laboratories.
INTERCONNECT MATERIALS METROLOGY (Priority 4)	<p>Characterization methods for thermal conductivity of nanometer scale thin films in both static and stressed conditions are needed. As the size of interconnects continues to decrease, the thickness of the Cu diffusion barriers must be reduced to minimize the impact of this layer on the interconnect resistance. Metrology and characterization capabilities are needed to determine the effectiveness of sub-2 nm novel materials in blocking the diffusion of Cu into the interlayer dielectric (ILD) and device regions. It is important to determine such variables as, the mechanisms for Cu diffusion through the barrier when they fail (i.e., pinholes vs. diffusion, etc.), and diffusion coefficient, etc.), and low k-metal interface structure and bonding. For example, there is a need to understand why molybdenum (Mo)-doped Ruthenium (Ru) thin films are thermally stable up to 725 °C, whereas those of a pure Ru film fail at a lower annealing temperature of 575 °C<sup>70</sup>.</p> <p>As transistor areal densities continue to increase and stacked die 3D integration schemes are considered to drive transistor densities even higher, heat dissipation through the metal interconnect is becoming an increasingly important consideration. Recent theoretical and experimental investigations have shown that the chemical bonding and detailed structures of interfaces can have a significant influence on thermal boundary resistance (TBR)<sup>71</sup>. Therefore, new methods for efficiently characterizing the TBR of the numerous interfaces present in low-k/Cu interconnects are needed, as well as research to better understand how the processes influencing interface formation and chemical bonding influence TBR.</p> <p>Through substrate via (TSV) has emerged as a leading technology for 3D integration schemes. New metrology is needed to characterize TSV enabled 3D system. For example, thermally induced defect formation and growth, as well as embedded materials degradation, affect the reliability of TSV. Any metrology to study TSVs must be capable of detecting discontinuities due to defects and material distortions in otherwise electrically contiguous structures<sup>72</sup>. Therefore, there is also a requirement for a measurement technique that fully characterizes stress evolution in 3D interconnects and the surrounding Si<sup>73</sup>.</p>
MONOLAYER CONFORMAL AND DETERMINISTIC DOPING (Priority 5)	For devices whose properties depend on the position of atoms in the channel, metrology for deterministic doping is required to confirm the presence, placement, and electronic state of individual dopants. Established continuum techniques, such as scanning probe based four-point probe, secondary ion mass spectroscopy (SIMS), and spreading resistance profiling (SRP), are still useful for characterizing ultra-shallow junctions formed by conformal doping. Ultra- shallow junction imaging techniques, i.e., scanning capacitance microscopy and scanning spreading resistance microscopy <sup>74</sup> , are also available. Single dopants can be imaged with scanning tunneling microscopy (STM) and low-temperature frequency-modulated Kelvin force microscopy <sup>75, 76</sup> . The STM technique, sensitivity is limited to the first 2 or 3 atomic layers. Atom probe tomography (APT) / local electron atom probe (LEAP) can provide detailed 3D atomic level images of the positions of all the atoms in the device <sup>77,78</sup> .
SIMULTANEOUS SPIN AND ELECTRICAL MEASUREMENTS (Priority 6)	Multiple emerging devices are based on control of spin as an alternate state variable including, but not limited to, spin transfer torque magnetic random access memory (STT-MRAM), nanoscale spin transistors, spin wave devices, hybrid-ferroelectric/magnetic structures, and other spin-based logic concepts. These require metrology that depends on understanding nonlinear device dynamics, coupling, and noise. For example, metrology is needed for spin currents and transport in multilayered / heterogeneous systems.
ULTRA-SCALED DEVICES (Priority 7)	<p>Emergent nanoscopic properties will introduce new failure mechanisms which will require trading device performance for reliability. Hence, new metrologies and models are needed to characterize the performance and reliability of emerging nano-scale devices. A thorough understanding of the sources of variability and their impact on device noise is critically needed for enabling the successful design and integration of emerging materials into nanoelectronics. This foundational need will drive the development of tools for identifying and characterizing the significant emergent sources of variability and noise in nanoscopic systems. There is a need to characterize and understand the aging of nano- materials and nanostructured devices, and the consequences of such aging on device performance since most of the existing data based on bulk material properties may not be applicable.</p> <p>The introduction of 3D device structures, requires imaging of a complex structures with atomic resolution of interfaces and chemistry. Furthermore, the integration of the newly introduced materials, such as high-k dielectrics in combination with metal-gate stack, needs careful optimization to produce excellent reliability<sup>79</sup>. This requires imaging of a complex 3D structure with atomic resolution of interfaces and chemistry. Some progress has been made in this regard; for example, using aberration corrected electron energy-loss spectroscopy, two-dimensional elemental and valence-sensitive imaging at atomic resolution, of a La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>/SrTiO<sub>3</sub> multilayer have been demonstrated, and the data show an asymmetry between the chemical intermixing on the manganese-titanium and lanthanum-strontium sublattices<sup>80</sup>. For 3D interconnects, penetration of x-rays provides a major advantage to nondestructively imaging a 3D volume<sup>81</sup>. Strategically, segmentation of 3D data allows objective, quantitative analysis of complex structures<sup>82</sup>. Further research work is needed to avoid distortions due to interactions between probes and the very thin films used.</p>
MOLECULAR DEVICES (Priority 8)	New metrology capabilities such as inelastic electron tunneling spectroscopy <sup>83</sup> , and backside FTIR <sup>84</sup> for the study of vibrational states, and techniques such as transition voltage spectra, STM, Conductive AFM, and Kelvin Probe AFM enable some understanding of transport through individual molecules and molecular interfaces. However, additional research is needed to develop new metrologies, such as nondestructive, in situ 3D methods, to characterize contact interactions with molecules and electronic properties of the embedded interfaces and molecules.

**Table ERM10C. Prioritized set of Metrology ERM Challenges and Needs**

An additional Metrology related ERM challenges and critical materials parameters includes 3D metrology for sub-10 nm structures.

## 10. MODELING AND SIMULATION

With device dimensions 14 nm or below, materials modeling or computational materials is becoming a critical part of technology development and is needed to address several components of technology development<sup>85</sup>:



- 1) Synthesis to structure & composition, especially on the interfaces and multi-interface material structures
- 2) Properties of these structures including interface physics of state transition, defects states, etc. In addition, non-equilibrium properties of these structures such as conductance, mobility,
- 3) Probe interactions with samples to enhance quantification of structure, composition, and properties.

### 10.1 DEVICE MODELING AND SIMULATION CAPABILITY NEEDS

With device dimensions continuing to shrink below 14nm, every device technology needs improved modeling capabilities to evaluate operating mechanisms and to optimize device structure. The material modeling needs for different Emerging Research Devices are identified, in Figure ERM8, from synthesis to prediction of properties. ERM Modeling and Simulation Needs (columns C-H) are those required to help in the viability of the device materials in a research environment. For devices that are potentially closer to industrial evaluation, the ERM has identified modeling needs for potential optimization of device structures (columns J-R).

*Structure–property relationships and fabrication enables faster learning.*

*Figure ERM8. Device Material Modeling and Simulation Challenges and Needs*

### 10.2 LITHOGRAPHY MODELING AND SIMULATION NEEDS

For Lithography material modeling, the ERM has focused on directed self-assembly (DSA) with block copolymers and the modeling needs are identified in Table ERM11E-F. As industry evaluates DSA as a potential technology to extend lithography beyond 10nm, new materials will be needed modeling is needed to aid in their evaluation. Clearly, modeling is needed to evaluate the potential for new high  $\chi$  materials to form defect free patterns and identify allowable variations in guide structures that can produce these. There is also a critical need for efficient computational models to be used in EDA tools to translate from design patterns to guide structures on masks that will be patterned on wafers. Multiple applications of DSA are being considered and the placement of guide structures must comprehend self-assembly effects, such as guide pattern density interactions) to minimize defects in the assembled patterns. ERM Modeling and Simulation Needs are those required to help in the viability of the DSA materials in a research environment. For DSA materials that are potentially closer to industrial evaluation, the ERM has identified modeling needs for potential optimization of patterning

structures.

### 10.3 INTERCONNECT MODELING AND SIMULATION NEEDS

Interconnects face critical challenges with needs for lower  $\kappa$  dielectrics, ultra-thin Cu diffusion barrier layers, and novel interconnect materials. Modeling and simulation capabilities are needed to evaluate some of the critical issues for each of these technologies. The important capabilities required to assess viability of an interconnect material or technology in research requires significant interaction between modeling with experiments to improve the accuracy of the modeling.

### 10.4 MODELING AND SIMULATION CAPABILITIES

With device dimensions approaching 10 nm, atomic- scale-based materials modeling or computational materials is becoming a critical part of technology development and is needed to address several components of technology development, as illustrated below; In the absence of modeling, empirical experimentation is used to characterize and drive technology development. This process is both expensive and time consuming. More importantly, the specific operating window identified experimentally may not be globally optimal. A faster rate of learning provides compelling reasons for materials modeling as with shrinking dimensions, device performance is very much driven material properties:

- 1) *Synthesis to structure & composition*, especially on the interfaces and multi-interface material structures
- 2) *Properties* of these structures including interface physics of state transition, defects states, etc. In addition, non- equilibrium properties of these structures such as conductance, mobility,
- 3) *Probe and metrology interactions* with samples to enhance quantification of structure, composition, and properties.

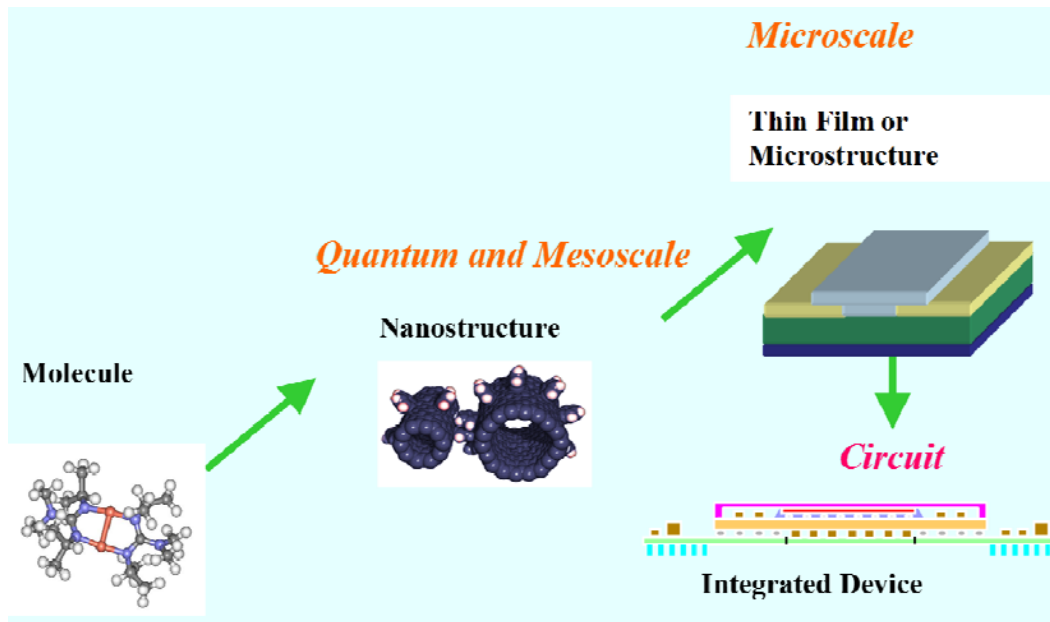
Materials modeling is applied at different levels based on the accuracy and the end application requirements. All material applications require simultaneous optimization of multiple properties such as electronic, mechanical, thermal, surface chemical reactivity, etc. If the dimensions of the materials are in nanometers, they are of the same order of magnitude as the domains in the materials such as grain sizes. These lead to nanomaterials possessing unique properties making them optimal candidates to enhance or replace conventional materials and approaches. However, the need for optimization of multiple properties requires models that correlate nanostructure to properties. There are multiple stages in which materials modeling can provide value in technology development. In the *first* stage during early material development, the need is to relate structure and chemistry to desired material properties. This is done in conjunction with a specific metrology and is used to characterize both structures and their properties. In addition the models are needed to optimize synthesis and transport processes including film growth. In the *second* stage, the models are applied to material improvement where they are used to optimize structure, composition, purity, and interfaces. Here as we have mentioned above, the models relate structure and composition to properties. In the *third* stage, models are used to relate material properties to the functional properties of the device. The properties of the resulting structure needed to be understood in terms of transport of electrons, phonons, and atoms. The models at this stage in conjunction with experimental observations are used to optimize synthesis and integration.

The behavior of devices and materials are directly correlated to their electronic structure and lattice physics. This is equally valid for both charge-based and non-charge-based technologies, as physical and chemical effects in these dimensions are directly related to the electronic structure. Physical modeling and numerical simulations are critical for multiple reasons:

1. *explain observed phenomena,*
2. *predict new phenomena,*
3. *direct experimental studies to desired outcomes,*
4. *interpret metrology.*

In addition, they provide fundamental understanding of both the mechanisms and the interactions between processes and materials.

Application of materials for ERM constitutes fundamental understanding and characterization of synthesis, structure, and properties. This is the natural logical flow for designing and integrating newer materials to develop structures whether it is for switching device, interconnects, or packaging. The method and conditions of synthesis



determine the structure and composition of the engineered materials. Structure in turn, determines the material properties and performance. As can be seen in Figure ERM9, models span multiple scales and need to be simulated using appropriate assumptions. The key intent of material simulation is to identify and quantify chemical knobs at the levels of atomic, nano, and thin film dimensions that modulate the behavior in the integrated devices.

*Materials form different important roles at different levels.*

**Figure ERM9.** Modeling from Molecules to Circuits

The complexity of materials modeling in nano dimensions is increasing due to increasing complexity from a variety of factors.

1. *Combinatorial Nature:* Number of materials has continued to increase with the development of several new material systems including high-k/metal gate, porous dielectrics, copper interconnects, and polymer materials for packages (leading to over 3X increase in number of elements over a period of 20 years). This effect is further augmented as materials are used in combinations estimated to be increase by more than 10X in number of material combinations over the same time period as above.
2. *Nanodimensions:* Most of the devices have dimensions close to material domain sizes (e.g. grain size, thin film thickness). As a result, the performance of the device is determined by the material properties at their characteristic dimensions. For example, Surface scattering is estimated to dominate interconnect resistivity for any metal as feature sizes are reduced to even smaller. In addition, with scaling, ratio of surface to

volume leads to interface properties determining overall behavior of devices unlike the bulk properties determined in the previous generations. In addition, smaller number of atoms in smaller dimensions leads to larger statistical variations.

3. *Topography*: For non-planar devices, topography of material structures modulates device behavior since the same single crystalline material may have multiple orientations dependent on the interfaces. This is further complicated by polycrystalline or amorphous materials with grain boundaries. These in turn lead to property variations.
4. *Topology* of the nanostructures and molecules. Electronic and phonon densities of states are determined by the chemical bonding and electronic band structures. Since the topology determines the functional properties of devices, efforts to analyze these effects are necessary both from characterization and modeling studies. For example, carbon nanotubes and graphene sheets demonstrate large conductivities and strong mechanical properties which can be affected by their orientation and topology.
5. *Correlated Properties* of strongly materials cannot be easily predicted from band theory given the nature of their interactions. This because traditional Density Functional Theory fails for these classes of materials. Another associated property is the metal-to-insulator transition. The complexity of physics is due to multiple mechanisms attributed for the transition<sup>86</sup>.

### 10.4.1 SYNTHESIS

Synthesis determines the structure and composition of thin films. To predict the material properties, we need both characterization and physical modeling of the relevant structures. The materials themselves may be crystalline, poly-crystalline, semi-crystalline, amorphous, or visco-elastic. Even in bulk materials, structure of the materials determines their behavior<sup>87</sup>. For example, the resistivity of films in a certain crystallographic orientation (100) is different from (111) orientation. Realistic structures are not ideal single crystalline films and need advanced metrology for their complete characterization including characterization of grain morphology and size.

Materials synthesis influences the material morphology and the desired end user application. For example, nanotube growth and functionalization are determined by the chemical and electrical conditions in the reactor and the interactions with the substrate. Depending on the method of synthesis, in-situ and ex-situ requirements are different. For example, in a low pressure process, ex-situ measurement may result in oxidation and altering of the properties of the film. From a modeling perspective, a key requirement is to understand roles/mechanism of processing and the specific structure resulting from the synthesis. As an example, in atomic layer deposition, the physical model must comprehend gas phase and surface chemistry in addition to mass and energy transport. Film nucleation and subsequent growth, which determine the morphology of the nanostructure and thin films, also require modeling. In addition to description of the temporal evolution of a new phase, it becomes necessary to describe the spatial ordering in many systems (eg. quantum dots, nano-wires<sup>88,89</sup>). Classical nucleation and growth concepts adequately describe phase transitions in some nanoscale phase change memory materials<sup>90</sup>.

Controlling the morphology of the nanoscopic material requires detailed information on phase stability and dynamics of atomistic processes. In small nanoscale systems in which dimensions may not be significantly larger than the range of interatomic interactions, classical thermodynamic concepts such as extensive and intensive properties may no longer be valid. In these cases, the classical concept of a phase transition, including the Gibbs Phase Rule that occurs in the thermodynamic limit of an infinitely large system, may not hold<sup>91, 92</sup>. Development of a theory of phase transition in such finite size systems for understanding the dynamics of phase transition may be critical to control nucleation and growth of certain nanoscale materials. Description and prediction of fragmentation, a process by which phase transitions have been observed to occur in nanoscopic systems, presents a significant challenge in statistical mechanics. Density functional theory<sup>93,94</sup> which is based on density fluctuations rather than existence of clusters of classical and atomistic nucleation should be investigated as a tool for describing phase transitions in small systems and fragmentation. Structures characterized based on synthesis methods serve as inputs into the physical models. Given the limited size of problems that can be solved, a combination of techniques spanning different length and time scales are needed to model structures effectively.

### 10.4.2 STRUCTURE AND PROPERTIES

The material properties themselves are based on the electronic band structure of condensed matter. For a given structure, the Schrödinger equation determines chemical, electrical, mechanical, and thermal properties. In turn, the number of electrons in the structure determines the nature of the hyper-dimensional Schrödinger equation. As the number of electrons are very high in condensed matter ( $\sim 10^{22}$  -  $10^{23}$  in an unit cubic centimeter of material), any solution of the equation for realistic macroscopic system is generally done using one of two simplified techniques; 1) single particle approximation and/or 2) multi-scale techniques with distinct formalisms representing different scales. The models themselves have different scales based on the specific physical phenomena. Atomic or molecular scale is based on self-consistent solutions of Schrödinger equation as mentioned above. Nanostructural scale uses multi-scale techniques based on kinetic and quantum formalism (e.g. device, or interconnect with barrier layers). The thin film scale (e.g. gate oxide or barrier layer) is mesoscale in nature, and links with kinetic models at the macroscopic level and atomic models at the microscopic level. In the macroscopic scale (e.g. die, package), bulk or effective properties are used in constitutive models that describe the response of materials to different stimuli. For the area of ERM, the main focus of research should be on the first three levels, with an emphasis on atomic or molecular and nanostructural scale. Since structural dimensions are currently at 32 nm or below, the materials properties at this scale may behave differently when integrated than in the bulk. In addition, optimization of the performance reliability of devices or materials in nano-dimensions during ambient and accelerated usage conditions requires model extension to include phonon interactions and other long time scale processes. More details of the other scales are covered in the Modeling and Simulation section in the roadmap.

The most widely used technique is the Density Functional Theory (DFT) in which the  $3N$  dimensional system is reduced to three dimensional problems for most of the ground state problems<sup>95,96</sup>. The approximations are generally of two types, one in which the density functions are systematically improved to capture more and more non-local features of the wave functions and the second one in which the exchange-correlation functional are approximated by analytical models (e.g. meta functionals). One of the most widely used approximations is the Local Density Approximation (LDA)<sup>97</sup> where local densities of  $N-1$  electrons are used to approximate the interaction potentials leading to a 3 dimensional problem. More accurate approximations such as Generalized Gradient Approximations (GGA)<sup>98,99</sup> are used to increase the applicability of the DFT methods. Yet the transferability of the exchange-correlation functional is a critical issue for application to variety of materials.

Most of the full quantum simulations or *ab-initio* simulations can be done for smaller systems up to 1000-5000 atoms, which are approximately about 30 cubic nanometers. The models which cover these domains are mostly based on quantum methods which solve Schrödinger equation in  $3N$  dimensions, where  $N$  is the number of electrons in the system. As mentioned above, most of the devices are in condensed matter,  $N$  is of the order of  $10^{22}$ . Different methods scale depending on the number of electrons or basis sets used in the approximation;  $O(N^3)$  for Density Functional Theory,  $O(N^4)$  for Hartree-Fock ( $N$  being the number of basis functions),  $O(N^7)$  for some coupled cluster calculations. This poses the problem in solvability of the equations for practical applications in both the chemistry (needed for synthesis) and materials analysis. Efficient algorithms for large-scale quantum-mechanical calculations with aid of parallel computing technology are developing<sup>100</sup>.

In addition, for materials, due to the complex properties (e.g. Mott transition, spin-orbital coupling), many-body theories are entering mainstream in applications<sup>101,102,103,104</sup>. Some examples of these higher-order approximation techniques are Green's Function techniques (GW), Quantum Monte Carlo, Path Integral methods etc. These techniques model both the equilibrium and non-equilibrium properties without mean field approximations as mentioned above. The first technique uses perturbation technique to comprehend many-body interactions in a self-consistent manner. The other techniques mentioned above model quantum phenomena in a variety of ways: 1) Solve the Schrödinger equation using statistical methods, or 2) Use Feynmann's path integral method for directly estimating properties. All these techniques are computationally intensive and are limited in the size of the physical problems to which they can be applied.

Due to the limitations of the above techniques, semi-empirical models for extending to larger systems of million atoms are viable alternatives. These techniques are characterized by a variety of techniques in which interaction energies are characterized by different potentials. The applicability of atomistic models can be increased to over 100 million atoms by using more of semi-empirical characterization like force fields. Some of the semi-empirical methods used for modeling materials include following:

1. Classical molecular dynamics which are based on interaction potentials formulated from quantum



#	ERM Related M&S Difficult Challenges
1	Extension to larger scales (tens of nanometers) for equilibrium calculation and temperature dependence of properties and processes.
2	Structure and thermodynamic phase equilibrium of nano-materials including poly-crystalline and disordered systems
3	Metallic systems specifically transition and inner transition metals.
4	More generalized extension for band gaps
5	Coupling of electronic structure predictions to non-equilibrium process such as transport and excitation
6	Lattice physics that includes atomic and ionic response to externally applied fields for both metrology and reliability
7	Extension or linking of quantum models from femtoseconds to microseconds or longer to emulate realistic synthesis and transport.

simulation. This technique has been widely applied to synthesis methods such Physical Vapor Deposition (Voter, ) and thermal properties<sup>105</sup>.

2. Hybrid techniques such as Born-Oppenheimer approximations where the electrons are treated using quantum formalism, while the ions are treated as classical. Further extensions of these techniques to self-consistent formalism include Car-Parrinello methods where dynamic motion of electrons and ions are set to reach equilibrium state.
3. Kinetic Monte Carlo methods which use energies estimated from *ab initio* methods or use classical potentials, are used to simulate time-dependent states of a system in a stochastic way. Unlike molecular dynamics, these methods do not calculate the dynamics of the system and

hence can be used to simulate longer time scales. The technique has been applied to nucleation<sup>106</sup>, and ultra-low pressure chemical vapor deposition<sup>107</sup>.

Although the above techniques have been demonstrated to be useful in certain applications, they still need to be scaled to meet realistic system sizes (~100 nanometers) and physical times (microseconds or seconds).

Despite recent advances, theory has many limitations that gate applicability to systems of practical interest for quantitative correlations. Current applications include: equilibrium energies, density of states, reaction rates, effects of defects in parts per thousand, and transport within nanostructures with interfaces. At the quantum scale, the current applicability of available models is rather limited. Difficult ERM related modeling and simulation challenges are rank ordered in Table ERM11B, below.

**Table ERM11B.** A prioritized list of ERM related difficult modeling and simulation challenges

With respect to the last difficult challenge, these extensions are specifically critical for molecular dynamics and Monte Carlo methods (both based on quantum and classical approaches). As a result, multi-scale techniques are becoming as more valid techniques depending on the nature of the system and the specific properties. One such set of relations between these models are given in Figure ERM10, below<sup>108</sup>.

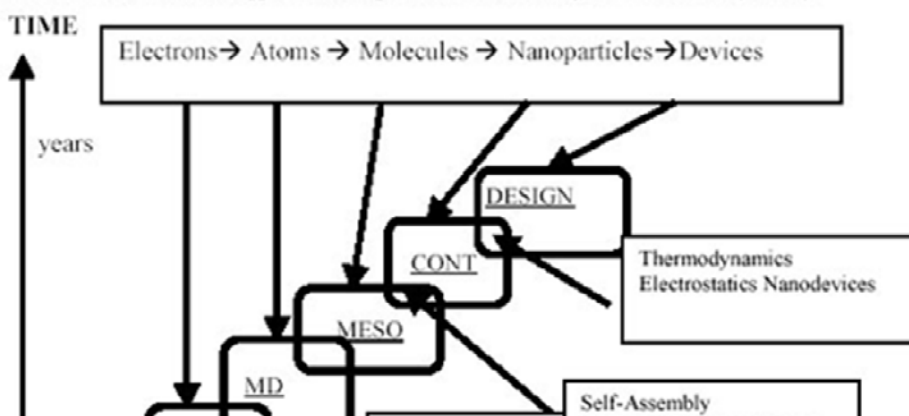
Figure ERM10. Multiscale Modeling

### 10.4.3 MODELING FOR METROLOGY AND CHARACTERIZATION

As mentioned previously, when new material properties are characterized, models must be developed to guide synthesis to further enable exploration of new structures and more complex interactions between materials. Establishment of an experimental database with results from well-characterized structures could accelerate the development of more accurate full ab initio and self-consistent reduced models. More quantitative material property mapping at the nanometer-scale requires development of models to probe interactions of nanostructured materials. Improved structure and property mapping for more accurate TEM, AFM, conductance AFM, Kelvin Probe AFM, Magnetic Force Microscopy (MFM) and other new techniques could improve development of nanometer scale material models. Simulations, which help to interpret metrology, would also improve these techniques.

Summarizing, the properties that need to be addressed from both modeling and metrology are summarized in Table ERM11C, below;

Figure 1: Multi-Scale Hierarchical Approach to Computational Nanotechnology and Molecular Engineering



Difficult ERM/Metrology Modeling Challenges	
<p><b>Electronic Properties (Metals, carbon, semiconductor &amp; insulators)</b></p> <ul style="list-style-type: none"> <li>a. Size &amp; structure dependence of</li> <li>b. Energy Levels including bandgap</li> <li>c. Spin-orbit coupling</li> <li>d. Density of States</li> <li>e. Long range forces including van der Waal's, etc.</li> </ul>	<p><b>Interface Properties</b></p> <ul style="list-style-type: none"> <li>a. Interface states</li> <li>b. Work functions</li> <li>c. Interface Transport and Scattering</li> <li>d. Debonding and chemical reactivity</li> <li>e. Surface Energy &amp; Defect Energy Levels</li> </ul>
<p><b>Optical Properties</b></p> <ul style="list-style-type: none"> <li>a. Real/imaginary optical constant matrixes for: Individual nanostructured materials; Matrixes of nanomaterials; Nanomaterials with ultra-thin film coatings</li> <li>b. Photo-chemical Reaction (UV Resistivity, Degradation mechanism.)</li> </ul>	<p><b>Transport properties</b></p> <ul style="list-style-type: none"> <li>a. Electrical conductivity and mobility (electron carrier lifetime)</li> <li>b. Thermal conductivity (phonon-lifetime)</li> </ul>
<p><b>Mechanical Properties</b></p> <ul style="list-style-type: none"> <li>a. Modulus, Yield Stress</li> </ul>	<p><b>Thermal properties</b></p> <ul style="list-style-type: none"> <li>a. Heat capacity</li> <li>b. Seebeck coefficient</li> </ul>

---

**Table ERM11C.** *Metrology Material Modeling and Simulation Challenges and Needs*

Please see Table ERM11, for a complete list of current ERM specific Materials Modeling and Simulation related difficult challenges and needs that the ERM and Modeling and Simulation teams plan to further refine in 2016-2017.

## 11. OUTSIDE SYSTEM CONNECTIVITY

Table ERM12 provides a set of top Outside System Connectivity material priorities for ERM.

Priority	ERM Related OSC Difficult Challenges
1	Plasmonic Materials to direct or focus photons
2	Photonic crystals for compact routing of photons in waveguides
3	Novel materials that change optical properties after being exposed to an optical signal
4	The ability to switch properties back with exposure to a different optical signal.

**Table ERM12.** *Prioritized Outside System Connectivity related ERM needs*

Additional OSC-ERM challenges and critical materials parameters include:

- Novel materials that enable optically based switching, routing and amplification
- Highly non-linear materials for optical regeneration and retiming
- Meta-materials and plasmonics that enable lower cost alignment of optical elements

## 12. POTENTIALLY DISRUPTIVE CONVERGENT APPLICATION OPPORTUNITIES FOR THE NEXT GENERATION OF EMERGING RESEARCH MATERIALS

As mentioned at the beginning of the chapter, 'the MtM domain requires a highly interdisciplinary set of expertise, e.g. electrical and mechanical engineering; as well as materials, biological, medical, energy, aerospace, transportation, communication, and sustainability sciences. The trend towards the convergence of monolithically integrated functional diversification with miniaturization manifests as increasing complexity in the road-mapping process.' With this update, the ERM team has begun to engage expert colleagues in Other Relevant Communities (ORCs) to identify a few synergistic and potentially disruptive convergent opportunities for the traditional ITRS community and colleagues in adjacent industries. Figure ERM11, below, conveys examples of Nature inspired complex functionality that can be monolithically integrated into a single compact system. These candidate technologies are based on complex systems, e.g., living cells, which serve as proof of principle for the monolithic

<b>Energy</b>	Generation Conversion Storage Utilization Architectures	<b>Processing and Bioelectronics</b>	Personalized Medical Diagnostics Prosthetics and Implantable Devices Biotic/Abiotic Interfaces Multiproperty Imaging Noninvasive [Tricorder-like]
<b>Sensing</b>	Physical Chemical Multimode Multiscale Subsurface	<b>Adaptive Coatings</b>	Dynamic Local Mapping Camouflage Obscuration Smart Physical Changes Remotely Directed Adaptations
<b>Actuation</b>	Analog Digital Hybrid Approaches Hard and Soft/Adaptive Systems Autonomous Emergent Behavior	<b>Fabrication, Disassembly, and Reuse</b>	Directed and Guided Processes Novel 3D Concepts Adaptive Methods Biomimetic Approaches Functionally/Application Guided
<b>Communication</b>	Transmission Filtering Novel A/D Interconversions Low Energy Approaches Reception	<b>Design Approaches</b>	DNA and Protein Analogs Overlapping Genes Adaptive and Epigenetic Designs Novel Concepts Functionality and Application Guided

**Figure ERM11.** Nature inspired monolithically integrated functionality<sup>109</sup>

integration of complex, interdependent, convergent, and useful functionality. Consider the commercial potential for one application of the bioelectronics element in this figure, i.e., blood tests. In 2013, worldwide semiconductor revenue reached \$300B. Given that the cost of blood tests is on the order of \$100-\$1000/test and ~7.3B people, the market opportunity for blood tests alone is roughly \$1T/year. Collaborative transdisciplinary research is needed to identify materials and processes that catalyze breakthrough and convergent advances in these technologies. Initiatives that leverage the expertise of colleagues in adjacent spaces who know the local environment, e.g., biology, energy, etc., will help to drive novel approaches and more optimal materials, process, manufacturing, and performance solutions to emerging IoT challenges than can be achieved by semiconductor centric approaches. Table ERM13 identifies several emerging application opportunities that will drive and enhance future ERM Working Group activities. Please note that this table represents a work in process. Consensus building is underway with colleagues in adjacent technologies to further refine the list of convergent challenges and to clarify the scope of each opportunity, so as to benefit all participants.

#	Convergent Challenges and Opportunities	Selected Potentially Disruptive Technologies that Require Breakthrough Advances in Emerging Research Materials
1	Mobile Communication and Information	Security; Ubiquitous and low power communication and information processing [OSC]; Optical switching for routing [OSC], Monolithically integrated smart nano-composite materials for enhanced functional density [HC], [HI]; Flexible electronics [HC], [HI]
2	Smart Transportation	Conventional and flexible displays; Price point; Smart and adaptive skins and structures [HC], [HI]
3	Big Data	Security; Robust and ubiquitous information storage, access and processing [OSC]; Deterministic systems [MM], [BC]; Quantum computation [BC], [HI]; Nature inspired information processing [BC]; Convergent neurosynaptic materials and systems [HC], [HI]
4	High performance, Sustainable, and Robust Materials, Chemistries and Manufacturing	Security; Functional DSA (PAT/LIT), Deterministic (PAT/LIT), Biocompatible (Healthcare/Pharma), Metamaterials (LIT), Adaptive Manufacturing (FI); Multiple-life cycle methods [HI]

5	Energy Technology	Secure, low power, self-powered systems; power distribution systems; Low energy manufacturing (FI); Integrated micro-fuel cells [HI]; integrated micro-batteries and super-capacitors [HC]
6	Medical/Health Care	Personalized diagnostics and ubiquitous monitoring; Prosthetics and implantable devices, with long term biotic/abiotic interfaces; Imaging [Intracellular to macroscopic]; Electronic physician and medical records; Telemedicine [HC], [HI]
7	Multi-functional Materials/Sensors	Convergent and monolithically integrated chemical, biological, physical, and NEMS platforms (MtM)

**Table ERM13.** Summary of potentially disruptive Emerging Research Materials application opportunities

## 13. TRANSITIONED MATERIALS

The ITRS 2.0 represents a strategic repositioning of the nanoelectronics community's scope, needs, and set of emergent opportunities. In alignment with this new perspective, this year's Emerging Research Materials (ERM) chapter assesses, prioritizes and repositions the traditional set of emerging research materials according to their relevance, potential insertion horizon, and likelihood for enabling ITRS 2.0 goals. Current ERMs are binned into one of three categories, i.e., tactical [T], strategic - near term [SNT], or strategic - long term [SLT]. Tactical materials are those current ERMs with potential insertion horizons of less than 9 years, as assessed by relevant Working Groups. These materials dominate the following transition tables. This year's chapter considers ERMs with 9-15 year potential insertion horizons as strategic-near term emerging research materials. Those SNT-ERMs now considered as strategic-near term materials by their parent working group, i.e., these teams deem the potential insertion horizon to be within 8 years, then these materials are positioned for transition out of the ERM chapter. Please refer to Table ERM13 for a draft list of Emerging Research Materials that are under transition consideration into and out of the ERM chapter.

### Table ERM14. Emerging Research Materials Transition Table

This chapter represents a work in transition. For this update, each Working Group and Focus Team has spent considerable effort and time to align its scope and requirements with the ITRS 2.0 vision. The ERM chapter will continue to refine and adapt its scope to engage with a new set of ERMs, many of which will be identified by this year's Working Groups and Focus Teams, as well as by colleagues.

## 14. REFERENCES

The set of references will be refreshed in the next chapter update, when the ITRS 2.0 teams have an opportunity to provide their inputs and assessments.

<sup>1</sup> C. Christensen, *The Innovator's Dilemma: When New Technologies Cause Great Firms to Fail* (Harvard Business School Press, Boston, 1997).

<sup>2</sup> <http://www.itrs.net/papers.html>

<sup>3</sup> Excerpted and adapted from the 2013 ITRS Executive Summary, *More than Moore*, p. 8

<sup>4</sup> Adapted from the 2013 ITRS, *Roadmapping Process*, p. 4

<sup>5</sup> Excerpted and adapted from the 2013 ITRS Executive Summary, *More than Moore*, p. 8

<sup>6</sup> K. Oyama, et al, "Extended scalability with self-aligned multiple patterning", 26th International Microprocesses and Nanotechnology Conference, November 5-8, 2013.

<sup>7</sup> E. van Setten et al, "NXE:3300B Platform – Imaging applications for Logic and DRAM," Proc. SPIE, 8886, 888604-1 (2013).

<sup>8</sup> Berggren et al, *Nano Lett.*, 13, 1555 –1558 (2013).

<sup>9</sup> J. Zhang et al Proc. of SPIE Vol. 9051 905111-1 (2014).

<sup>10</sup> M. Scotuzzi et al, *J. Micro/Nanolith. MEMS MOEMS* 14(3), 031206 (2015).

<sup>11</sup> L. Sun, W. Wang, G. Beique, et al., "Application of Frequency Domain Line Edge Roughness Characterization Methodology in Lithography," 29th Conference on Metrology, Inspection, and Process Control for Microlithography, Proceedings of SPIE, **9424**, # 942404, 2015.

<sup>12</sup> L. Sun, *et al.* "Application of frequency domain line edge roughness characterization methodology in lithography

- 
- " Proc. SPIE 9424, Metrology, Inspection, and Process Control for Microlithography XXIX, 942404.
- <sup>13</sup> L. Sun, *et al.* "Line edge roughness frequency analysis during pattern transfer in semiconductor fabrication", J. Micro/Nanolith. MEMS MOEMS. 14(3), 033501
- <sup>14</sup> (a) Chris A. Mack. "Understanding the efficacy of linewidth roughness post-processing ", Proc. SPIE 9425, Advances in Patterning Materials and Processes XXXII, 94250J.; (b) C. A. Mack, "Understanding the efficacy of linewidth roughness postprocessing," J. Micro/Nanolith. 2015, 14(3), 033503.
- <sup>15</sup> J. Jussot, E. Pargon, B. Icard, J. Bustos, and L. Pain. "Line width roughness reduction strategies for patterns exposed via electron beam lithography ", Proc. SPIE 9054, Advanced Etch Technology for Nanopatterning III, 905405.
- <sup>16</sup> M. Fouchier, E. Pargon, B. Bardet, "A new method based on AFM for the study of photoresist sidewall smoothening and LER transfer during gate patterning." Proceedings of SPIE, **8685**, 86850B, 2013.
- <sup>17</sup> M. Fouchier and E. Pargon "Atomic force microscopy study of photoresist sidewall smoothing and line edge roughness transfer during gate patterning", J. Micro/Nanolith. MEMS MOEMS. 12(4), 041308.
- <sup>18</sup> K. Xu, *et al.* "Key contributors for improvement of line width roughness, line edge roughness, and critical dimension uniformity: 15 nm half-pitch patterning with extreme ultraviolet and self-aligned double patterning", J. Micro/Nanolith. MEMS MOEMS. 12(4), 041302.
- <sup>19</sup> E. Pargon, *et al.* "Smoothing mechanisms involved in thermal treatment for linewidth roughness reduction of 193-nm photoresist patterns", J. Vac. Sci. Technol. B 31, 061203 (2013).
- <sup>20</sup> L. Azarnouche, *et al.* "Plasma treatments to improve line-width roughness during gate patterning", J. Micro/Nanolith. MEMS MOEMS. 12(4), 041304.
- <sup>21</sup> P. De Schepper, *et al.* "Line edge and width roughness smoothing by plasma treatment ", Proc. SPIE 8685, Advanced Etch Technology for Nanopatterning II, 868508.
- <sup>22</sup> P. De Schepper, *et al.* "Line edge and width roughness smoothing by plasma treatment", J. Micro/Nanolith. MEMS MOEMS. 13(2), 023006.
- <sup>23</sup> S. Matsumaru, *et al.* "Development of EUV chemically amplified resist which has novel protecting group", Proc. SPIE 9425, Advances in Patterning Materials and Processes XXXII, 94250U.
- <sup>24</sup> J. Jiang, M. O. Thompson, and C. K. Ober. "Line width roughness reduction by rational design of photoacid generator for sub-millisecond laser post-exposure bake ", Proc. SPIE 9051, Advances in Patterning Materials and Processes XXXI, 90510H.
- <sup>25</sup> M. Hori, *et al.* "Novel EUV resist development for sub-14nm half pitch ", Proc. SPIE 9422, Extreme Ultraviolet (EUV) Lithography VI, 94220P.
- <sup>26</sup> Y. Ekinici, M. Vockenhuber, N. Mojarad, and D. Fan. "EUV resists towards 11nm half-pitch ", Proc. SPIE 9048, Extreme Ultraviolet (EUV) Lithography V, 904804.
- <sup>27</sup> M. Shiratani, *et al.* "Novel EUV resist materials for 16nm half pitch and EUV resist defects ", Proc. SPIE 9048, Extreme Ultraviolet (EUV) Lithography V, 90481D.
- <sup>28</sup> R. Del Re, *et al.* "Low-LER tin carboxylate photoresists using EUV ", Proc. SPIE 9422, Extreme Ultraviolet (EUV) Lithography VI, 942221.
- <sup>29</sup> A. Frommhold, *et al.* "Towards 11nm half-pitch resolution for a negative-tone chemically amplified molecular resist platform for extreme-ultraviolet lithography ", Proc. SPIE 9425, Advances in Patterning Materials and Processes XXXII, 942504.
- <sup>30</sup> W. Shibayama, *et al.* "EUV lithography and etching performance enhancement by EUV sensitive Si hard mask (EUV Si-HM) for 1Xnm hp generation ", Proc. SPIE 9051, Advances in Patterning Materials and Processes XXXI, 905116.
- <sup>31</sup> Y. Borodovsky, 2012 International Workshop on EUV Lithography, Maui, Hawaii, June 4-8, 2012.
- <sup>32</sup> S. Sivakumar, "Enabling Production beyond 22nm", LithoVision 2013, San Jose, CA, Feb. 24, 2013.
- <sup>33</sup> F. Bornebroek, "Extending ArFi immersion scanner capability in support of 1xnm production nodes," SPIE Advanced Lithography, San Jose, CA, Feb. 27, 2014.
- <sup>34</sup> H. Egashira, Y. Uehara, Y. Shirata, Y. Shibazaki, J. Ishikawa, T. Funatsu, M. Ohba. Proc. SPIE 9052, 90521F, 2014.
- <sup>35</sup> Q. Peng, *et al.* "Nanoscale Patterned Materials with Tunable Dimensions via Atomic Layer Deposition on Block Copolymers," Adv. Mater. 2010, 22, 5129-5133.
- <sup>36</sup> W. Jung, *et al.*, "Patterning with amorphous carbon spacer for expanding the resolution limit of current lithography tool", Proc. SPIE, Vol. 6520, 65201C, 2007.
- <sup>37</sup> C. Bencher, *et al.*, "22nm Half-Pitch Patterning by CVD Spacer Self Alignment Double Patterning (SADP)", Proc. SPIE, Vol. 6924 69244E, 2008.

- <sup>38</sup> D. Guerrero, et al. "Material development for DP processes," Immersion Symposium, The Netherlands, Sept. 22-25, 2008.
- <sup>39</sup> M. Hyatt, et al. "Anti-spacer double patterning," Proc. SPIE 9051, 905118, 2014.
- <sup>40</sup> S. M., George. "Atomic Layer Deposition: An Overview", Chem. Rev. 2010, 110, 111-131.
- <sup>41</sup> C. Wallace, "Material Requirements for Self-Aligned Patterning – a Lithographer's Perspective", AVS 61st International Symposium & Exhibition, Baltimore, MD, Nov. 12, 2014.
- <sup>42</sup> C.G. Takoudis et al. J. Vac. Sci. Technol. A 2014, 32, 010601-1.
- <sup>43</sup> S. F. Bent, *et al.* "New Resist for Area Selective Atomic and Molecular Layer Deposition on Metal–Dielectric Patterns", J. Phys. Chem. C 2014, 118, 10957–10962; and references therein.
- <sup>44</sup> R. Hourami, et al. "Selective Deposition through Organic Blocking Layers", AVS 61st International Symposium & Exhibition, Baltimore, MD, Nov. 12, 2014.
- <sup>45</sup> Reference to ITRS roadmap on <0.01 defects/cm<sup>2</sup>
- <sup>46</sup> Reference to ITRS roadmap on Metals < 1 ppb
- <sup>47</sup> Reference to ITRS roadmap on Photospeed control
- <sup>48</sup> R. Coons, "Electronic chemicals: New materials keep Moore's Law on track", Chemical Week, June 30, 2014.
- <sup>49</sup> "IMEC and JSR team up for EUV", ElectronicsWeekly.com, May 18, 2015, <http://www.electronicweekly.com/news/manufacturing/imec-jsr-team-euv-2015-05/>
- <sup>50</sup> M. Harumoto ; J. Yoshida ; H. Stokes ; Y. Tanaka ;T. Miyagi ; K. Kaneyama ; C. Pieczulewski ; M. Asai, "Fundamental study of spin-coating using in-situ analysis and simulation", Proc. SPIE 9425, 94250G (March 20, 2015); doi:10.1117/12.2085277
- <sup>51</sup> T. Lan, J.M. Torkelson, "Methacrylate-based Polymer Films useful in Lithographic Applications Exhibit Different Glass Transition Temperature-Confinement Effects at High and Low Molecular Weight," Polymer, 55, 1249-1258 (2014).
- <sup>52</sup> C. Tang et al., "Non-Topcoat Resist and Defect Reduction," LithoVision 2013.
- <sup>53</sup> S. Chauhan, M. Somervell, M. Carcasi, S. Scheer, R. T. Bonnacaze, C. Mack and C. G. Willson , "Particle Generation during Photoresist Dissolution", Proc. of SPIE Vol. 7639, 763933 (2010).
- <sup>54</sup> P. A. Rincon Delgadillo, "Origin Of Defects In Directed Self-Assembly Of Diblock Copolymers Using Feature Multiplication", Ph.D Thesis, 2014 KU Leuven, Science, Engineering & Technology, 2014, ISBN 978-94-6018-837-4.
- <sup>55</sup> "Thermodynamic and Kinetic Aspects of Defectivity in Directed Self-Assembly of Cylinder-Forming Diblock Copolymers in Laterally Confining Thin Channels", B. Kim, N. Laachi, K. T. Delaney, M. Carilli, E. J. Kramer, and G. H. Fredrickson, J. Appl. Polym. Sci., 131, 40790 (2014).
- <sup>56</sup> S.-W. Chang, J. P. Evansc , S. Ge , V. V. Ginzburg, J. W. Kramer, B. Landes, C. Lee, G. Meyers, D. J. Murray, J. Park, R. Sharma, P. Trefonas III, J. D. Weinhold, J. Zhang, and P. D. Hustad, "New Materials and Processes for Directed Self-Assembly", Proc. of SPIE Vol. 8680, 86800F (2013).
- <sup>57</sup> H. Pathangi ; B. T. Chan ; H. Bayana ; N. Vandebroek ;D. Van Den Heuvel ; L. Van Look ; P. Rincon-Delgadillo ; Yi Cao; J.H. Kim ; G. Lin ; D. Parnell ; K. Nafus ; R. Harukawa ; I. Chikashi ; M. Polli ; L. D'Urzo ; R. Gronheid ; P. Nealey , "Defect mitigation and root cause studies in 14 nm half-pitch chemo-epitaxy directed self-assembly LiNe flow", J. Micro/Nanolith. MEMS MOEMS. 14(3), 031204 (Jul 02, 2015).doi:10.1117/1.JMM.14.3.031204
- <sup>58</sup> L. D'Urzo; W. Schollaert, X. Buch; H. Stokes, Y. Thouroude, "A Comprehensive Approach for Micro and Multiple Bridge Mitigation in Immersion Photolithography", Proc. SPIE 9425, 94251Y (20 March 2015); doi:10.1117/12.2085627.
- <sup>59</sup> P. Trefonas III, R. Carey, "Point-of-use purification", US Pat. 5350714 (1994).
- <sup>60</sup> T. Umeda, T. Yamanaka, N. Iguchi, S. Tsuzuki, "Microbridge reduction in negative tone imaging at photoresist point-of-use filtration", Proceedings of SPIE Vol. 9425 942521 (2015).
- <sup>61</sup> C. Park, J. Yoon, and E. L. Thomas, "Enabling nanotechnology with self assembled block copolymer patterns," Polymer, 44(22), 6725-6760 (2003).
- <sup>62</sup> G. M. Perera, C. Wang, M. Doxastakis, R. J. Kline, W.-l. Wu, A. W. Bosse, and G. E. Stein, "Directed Self-Assembly of Lamellar Copolymers: Effects of Interfacial Interactions on Domain Shape," *ACS Macro Lett.*, vol. 1, pp. 1244–1248, 2012.
- <sup>63</sup> M. Fernandez-Regulez, L. Evangelio, M. Lorenzoni, J. Fraxedas, F. Perez-Murano "Sub-10 nm Resistless Nano lithography for Directed Self-Assembly of Block Copolymers" ACS Applied Materials & Interfaces 6(23) pp21596-21602, 2014
- <sup>64</sup> L. Van Look; P. R. Delgadillo; Y.-t. Lee, "High throughput grating qualification of directed self-assembly patterns

---

using optical metrology" *Microelectronic Engineering*, 123 pp175-179, 2014

<sup>65</sup> C. Simao, D Tuchapsky, W. Khunsin, A. Amann, M.A. Morris, C. M. Torres, Defect Analysis and Alignment Quantification of Line Arrays Prepared by Directed Self-assembly of a Block Copolymer Proc. SPIE 9050, pp 905028-1 -10, 2014

<sup>66</sup> Q. Zhang, R. Li, R. Yan, T. Kosel, H. G. Xing, A. C. Seabaugh, K. Xu, O. A. Kirillov, D. J. Gundlach, C. A. Richter, and N. V. Nguyen, "A Unique Photoemission Method To Measure Semiconductor Heterojunction Band Offsets," *Appl. Phys. Lett.*, vol. 102, pp. 012101, 2013.

<sup>67</sup> T. M. Wallis, S. H. Lim, J. Chisum, Z. Popovic, and P. Kabos, "Near-field Antenna as a Scanning Microwave Probe for Characterization of Materials and Devices," in *Proceedings of the Fourth European Conference on Antennas and Propagation (EuCAP)*, pp. 1895185-1 to 1895185-3, 2010, Barcelona, Spain.

<sup>68</sup> Z. Wang, M.I A. Kelly, Z.-X. Shen, L. Shao, W.-K. Chu, and H. Edwards, "Quantitative measurement of sheet resistance by evanescent microwave probe," *Appl. Phys. Lett.* vol. 86, pp. 153118, 2005.

<sup>69</sup> A. Venugopal, L. Columbo, and E. M. Vogel, "Issues With Characterizing Transport Properties Of Graphene Field Effect Transistors," *Solid State Communications*, vol. 152, pp. 1311-1316, 2012.

<sup>70</sup> K.-C. Hsua, D.-C. Pernga, and Y.-C. Wanga, "Robust Ultra-Thin Rumo Alloy Film As A Seedless Cu Diffusion Barrier," *J. Alloys and Compounds*, vol. 516, pp. 102-106, 2012.

<sup>71</sup> G. Balasubramanian and I. Puri, "Heat Conduction Across A Solid-Solid Interface: Understanding Nanoscale Interfacial Effects On Thermal Resistance," *Appl. Phys. Lett.*, vol. 99, pp. 13116, 2011.; P. Singh, M. Seong, and S. Sinha, "Detailed Consideration Of The Electron-Phonon Thermal Conductance At Metal-Dielectric Interfaces," *Appl. Phys. Lett.*, vol. 102, pp. 181906, 2013.; J. Chen, G. Zhang, and B. Li, "Thermal Contact Resistance Across Nanoscale Silicon Dioxide And Silicon Interfaces," *J. Appl. Phys.*, vol. 112, pp. 64319, 2012.; M. Losego, M. Grady, N. Sottos, D. Cahill,

<sup>72</sup> C. Okoro, P. Kabos, J. Obrzut, K. Hummler, Y. S. Obeng, "Accelerated Stress Test Assessment Of Through-Silicon Via Using Rf Signals," *IEEE Trans. on Electron Devices*, Vol. 60, pp. 2015 - 2021, 2013.

<sup>73</sup> C. Okoro, L. E. Levine, R. Xu, J. Z. Tischler, W. Liu, O. Kirillov, K. Hummler, and Y. Obeng, "X-Ray Micro-Beam Diffraction Determination Of Full Stress Tensors In Cu TSVs," in Proc. *IEEE Electronics Components And Technology Conference (ECTC)*, Las Vegas, May 2013, Pp. 648 - 652

<sup>74</sup> L. Zhang, K. Hara, A. Kinoshita, T. Hashimoto, Y. Hayase, M. Kurihara, D. Hagishima, T. Ishikawa, S. Takeno, "Direct Visualization of Anomalous-Phosphorus Diffusion in Failure-Bit Gates of SRAM-Load pMOSFETs with High-Resolution Scanning Spreading Resistance Microscopy," in *Proceedings of the IEEE IEDM*, 2010, pp. 804.

<sup>75</sup> M. Ligowski, D. Moraru, M. Anwar, T. Mizuno, R. Jablonski, M. Tabe, "Observation of individual dopants in a thin silicon layer by low temperature Kelvin Probe Force Microscope," *Appl. Phys. Lett.*, vol.93, pp. 142101, 2008.

<sup>76</sup> R. Nowak, D. Moraru, T. Mizuno, R. Jablonski, M. Tabe, "Effects of deep-level dopants on the electronic potential of thin Si pn junctions observed by Kelvin probe force microscope," *Appl. Phys. Lett.*, vol.102, pp. 083109, 2013.

<sup>77</sup> K. Inoue, F. Yano, A. Nishida, H. Takamizawa, T. Tsunomura, Y. Nagai and M. Hasegawa, "Dopant distributions in n-MOSFET structure observed by atom probe tomography," *Ultramicroscopy*, vol.109, pp. 1479, 2009.

<sup>78</sup> K. Inoue, A. K. Kambham, D. Mangelinck, D. Lawrence, and D. J. Larson, "Atom-probe-tomographic Studies on Silicon-Based Semiconductor Devices," *Microscopy Today*, vol. 20, pp. 38, 2012.

<sup>79</sup> C. Auth et. al., "A 22nm High Performance and Low-Power CMOS Technology Featuring Fully-Depleted Tri-Gate Transistors, Self-Aligned Contacts and High Density MIM Capacitors," *Symposium on VLSI Technology Digest of Technical Papers*, pp. 131-132, 2012.

<sup>80</sup> D. A. Muller, L. Fitting Kourkoutis, M. Murfitt, J. H. Song, H. Y. Hwang, J. Silcox, N. Dellby, and O. L. Krivanek, "Atomic-Scale Chemical Imaging Of Composition And Bonding By Aberration-Corrected Microscopy," *Science*, vol. 319, pp 1073, 2008.

<sup>81</sup> C. Okoro, L. E. Levine, R. Xu, Ruqing; K. Hummler, Y. Obeng, "Synchrotron-based measurement of the impact of thermal cycling on the evolution of stresses in Cu through-silicon vias" *J. Appl. Phys.*, 115 (24), 243509, 2014

<sup>82</sup> L. W. Kong and A. C. Diebold, "Applying X-Ray Microscopy As A Void Inspection Technique For Through Silicon Vias," CNSE Albany, NY, *Fraunhofer Workshop On Stress Management For 3D IC'S Using Through Silicon Vias*, Oct 20, 2010

<sup>83</sup> J.G. Kushmerick, J. Lazorcik, C.H. Patterson, R. Shashidhar, D.S. Seferos, and G.C. Bazan, "Vibronic contributions to charge transport across molecular junctions," *Nano Letters*, vol. 4, pp. 639-642, 2004.; W.Y. Wang, T. Lee, I. Kretschmar, M.A. Reed, "Inelastic electron tunneling spectroscopy of an alkanedithiol self-assembled monolayer," *Nano Letters*, vol. 4, pp. 643-646, 2004.



- 
- <sup>84</sup> C.A. Richter, C.A. Hacker, L.J. Richter, “Electrical and spectroscopic characterization of metal/monolayer/Si devices,” *J. Phys. Chem. B*, vol. 109, pp. 21836-21841, 2005.
- <sup>85</sup> S. Shankar, “*Top 10+ Challenges for Enabling Computational Materials Design – A Nanotechnology Perspective*,” in *International Center for Materials Research (ICMR) Summer School on Materials Modeling from First Principles*, Keynote Lecture, University of California, Santa Barbara, USA, July pp. 19-31, 2009.
- <sup>86</sup> D. Jacob, K. Haule, and G. Kotliar. “Dynamical mean-field theory for molecular electronics: Electronic structure and transport properties.” *Phys. Rev B*, vol. 82, pp. 195115, 2010.
- <sup>87</sup> E. Kaxiras, *Atomic and Electronic Structure of Solids*, Cambridge University Press, Cambridge UK, 2003, pp. 1-676.
- <sup>88</sup> R. S. Berry. “Phases and phase changes of small systems,” in *Theory of Atomic and Molecular Clusters*, J. Jellinek, Ed. Springer-Verlag, Berlin, Germany, 1999, pp. 1-26.
- <sup>89</sup> Z. Wu, J. B. Neaton, and J. C. Grossman, “Charge Separation in Strained Silicon Nanowires,” *Nano Lett.*, vol. 9, pp 2418–2422, 2009.
- <sup>90</sup> S. Senkader and C. D. Wright. “Models for Phase-Change of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> in Optical and Electrical Memory Devices.” *J. of Appl. Phys.*, vol. 95, pp. 504, 2004.
- <sup>91</sup> T. L. Hill, “A Different Approach to Nanothermodynamics,” *Nanoletters*, vol. 1, pp. 273, 2001.
- <sup>92</sup> G. A. Mansoori, *Principles of Nanotechnology: Molecular Based Study of Condensed Matter in Small Systems*, World Scientific, Singapore, 2005.
- <sup>93</sup> J. W. Cahn and J. E. Hilliard. “Free Energy of a Nonuniform System. III. Nucleation in a Two-Component Incompressible Fluid.” *J. Chem. Phys.*, vol. 31, pp. 688, 1959.
- <sup>94</sup> D. W. Oxtoby. “Nucleation of First-Order Phase Transitions.” *Acc. Chem. Res.*, vol. 31, pp. 91, 1998.
- <sup>95</sup> P. Hohenberg and W. Kohn. “Inhomogeneous Electron Gas.” *Phys. Rev.*, vol. 136, pp. B864–B871, 1964.
- <sup>96</sup> W. Kohn and L.J. Sham. “Self Consistent Equations Including Exchange and Correlation Effects.” *Phys. Rev.*, vol. 140, pp. A1133-A1138, 1965.
- <sup>97</sup> J.P. Perdew and A. Zunger, “Self-interaction correction to density functional approximations in many body theory,” *Phys. Rev. B*, vol. 23, pp. 5048-5077, 1981.
- <sup>98</sup> J. P. Perdew and Y. Wang, “Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation,” *Phys. Rev. B*, vol. 33, pp. 8800-8802, 1986.
- <sup>99</sup> J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” *Phys. Rev. Lett.*, vol. 77, pp. 3865–3868, 1996.
- <sup>100</sup> A. Nakano, et.al., “A divide-and-conquer/cellular-decomposition framework for million-to-billion atom simulations of chemical reactions,” *Computational Materials Science*, vol. 38, pp. 642–652, 2007.
- <sup>101</sup> J. C. Grossman, L. Mitás, and K. Raghavachari, “Structure and Stability of Molecular Carbon: Importance of Electron Correlation.” *Phys. Rev. Lett.*, vol. 75, pp. 3870–3873, 1995.
- <sup>102</sup> J. Shumway, A. Franceschetti, and Alex Zunger, "Correlation Versus Mean-Field Contributions to Excitons, Multi-Excitons, and Charging Energies in Semiconductor Quantum Dots." *Phys. Rev. B*, vol.63, pp. 155316, 2001.
- <sup>103</sup> M. S. Hybertsen and S. G. Louie. “First-Principles Theory of Quasiparticles: Calculation of Band Gaps in Semiconductors and Insulators.” *Phys. Rev. Lett.*, vol. 55, pp. 1418, 1985; M. S. Hybertsen and S. G. Louie. “Electron Correlation in Semiconductors and Insulators: Band Gaps and Quasiparticle Energies.” *Phys. Rev. B*, vol. 34, pp. 5390, 1986.
- <sup>104</sup> G.W. Kotliar, D. Volhardt, Strongly-Correlated Materials Insights from Dynamical Mean Field-Theory, *Physics Today*, pp. 53-59, 2004.
- <sup>105</sup> B. C. Wood and N. Marzari, “Dynamics and Thermodynamics of a Novel Phase of NaAlH<sub>4</sub>,” *Phys. Rev. Lett.*, vol. 103, pp.185901, 2009.
- <sup>106</sup> Z. Wang and Y. Li, “Modeling Cu thin film growth,” *Thin Solid Films*, vol. 365, pp. 201-210, 2000.
- <sup>107</sup> D. G. Coronell, D. E. Hansen, A. F. Voter, C.-L. Liu, X.-Y. Liu, and J. D. Kress. “Molecular Dynamics-Based Ion-Surface Interaction Models for Ionized Physical Vapor Deposition Feature Scale Simulations.” *Appl. Phys. Lett.*, vol. 73, pp. 3860, 1998.
- <sup>108</sup> T. Cagin, J. Che, Y. Qi, Y. Zhou, E. Demiralp, G. Gao, and W. A. Goddard III, “Computational materials chemistry at the nanoscale,” *Journal of Nanoparticle Research*, vol. 1, pp. 51–69, 1999.

---

<sup>109</sup> Updated from *D. Herr, Invited presentation, SRC SemiSynBio Workshop, February 2013*