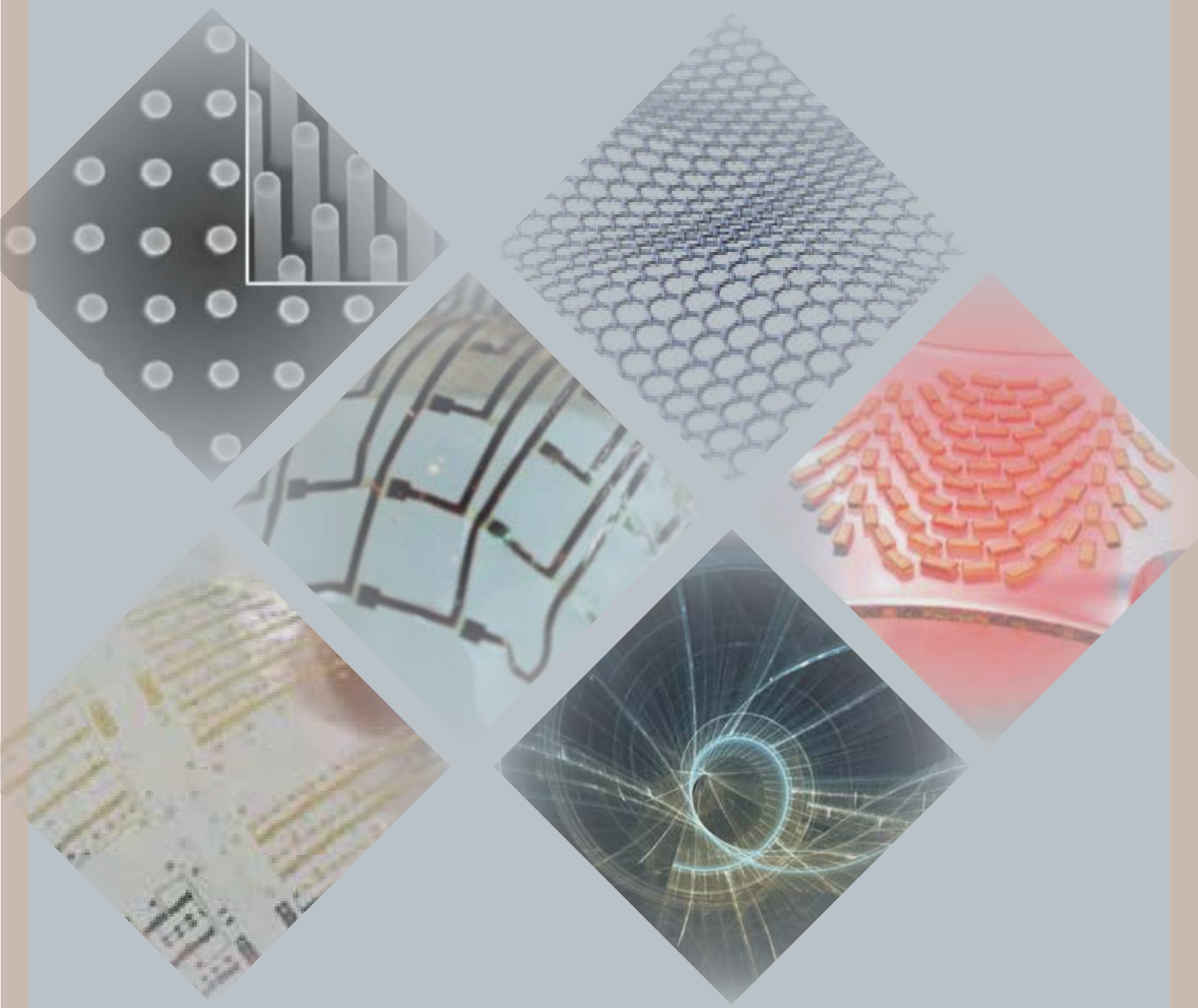
Current Challenges and Future Opportunities in

Electronic and Photonic Materials



NSF-EPM Workshop | September, 25-26, 2017

https://sites.cns.utexas.edu/epm_nsf_workshop

Workshop Report

Current Challenges and Future Opportunities in Electronic and Photonic Materials

NSF-EPM Workshop held on September 25-26th, 2017

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Table of Contents

1. Overview

Materials are so essential to societal advance that early civilizations are often named after a particular material (e.g. "Bronze age" and "Iron age"). Pivotal materials at the foundation of our modern civilization are far too diverse to name just a few. Electronics and photonics, nevertheless, capture the key technologies and industries that influence every aspect of our life, such as computing, communication, and health care. Advances in photonic and electronic materials thus bring unquestionable societal benefit in catalyzing revolutionary changes and transforming the platform that technologies are built on.

The Electronic and Photonic Materials (EPM) program at NSF plays a unique and vital role. The program bridges synthesis of various materials and fundamental condensed matter physics, while keeping in perspective potential applications in the electronic and photonic industry. In a sense, this program serves to link DMR condensed matter physics program and EECS. The program focuses on fundamental materials science including theory and modeling, growth, and characterization of a broad range of materials. Materials span semiconductors, oxides, magnetic and ferroelectric materials, organic materials, and van der Waals materials among others. Synthesis methods include molecular beam epitaxy (MBE), colloidal synthesis, chemical vapor depositions (CVD), and atomic layer deposition (ALD) combined with various nanofabrication programs exploring novel concepts such as metamaterials. Characterization efforts include various electron microscopies, scanning probes, transport measurements and optical spectroscopy studies. Computations and simulation research are often supported jointly with experimental investigations.

To solicit input from the community and to provide feedback to various funding agencies, a panel of experts working in the area of EPMs convened for a workshop. The goals of the workshop were threefold: (i) to better understand what the community views as current frontiers and future opportunities for electronic and photonic materials research; (ii) to learn what is the community's readiness to address important national issues and societal needs; and (iii) to identify gaps and new areas for EPM research in the near future.

Instead of trying to provide a brief overview of an exhaustive list of materials, the workshop was designed to focus on a few representative material systems. More specifically, the scope of the workshop encompassed epitaxially grown materials (semiconductors, oxide, and hybrid materials), van der Waals (vdW) materials, organic/flexible materials, and metamaterials. Effective material development requires integrated effort of computation, synthesis, characterization, and prototype device analysis. Workshop participants covered these different aspects of materials science to provide a comprehensive perspective.

The four classes of materials were chosen based on an analysis of the current funding portfolio of the EPM program and the programs of international conferences relevant to EPMs. We aimed to strike a balance between materials (epitaxially grown materials and flexible materials) that are relatively well established and have already made significant impact on electronic and photonic industries and the emerging materials that the community is actively engaged in investigating (van der Waals materials and metamaterials). While it is too early to identify the most compelling applications of these emerging materials, the community is generally optimistic that the

fundamental knowledge obtained in investigating these new classes of materials has the potential to bring transformative impact. The ultimate goal in material research is to catalyze technological advances. Thus, representatives from industry were also invited to provide necessary input.

The workshop programs and more detailed descriptions of the expertise of the participants can be found at the following website [https://sites.cns.utexas.edu/epm_nsf_workshop]. In advance of the workshop, each working group leader solicited input from members of their groups. At the workshop, the discussion leader gave an overview presentation that provided background and context, presented recent breakthroughs and highlighted outstanding challenges in the topic area. Each group then debated the best approaches to address these challenges and identified promising future directions. The outcomes of each working group discussion were presented to all participants, who then discussed cross-cutting areas and connections between the EPM program with various national initiatives. This report reflects the discussions that occurred during the workshop; omission of particular research areas should not be taken as a comment on their relevance or importance.

2. Executive summary

We provide a brief summary of the detailed reports generated by each working group. In addition to the four material classes, perspectives from industrial participants is summarized in a separate section. Connections between research activities supported by EPM programs and other national initiatives are then discussed.

2.1 *Epitaxially grown materials*

Epitaxial growth occurs in highly controlled environment (extreme high vacuum and stable temperature), leading to single crystalline materials that have advanced the frontiers of high performance electronic and photonic devices for decades. Epitaxially grown semiconductors and their heterostructures have enabled many discoveries of new quantum physics and have dominated high speed transistors, modulators and photovoltaics in the most demanding applications. The atomic level control of materials in epitaxial growth enable exquisite control of many degrees of freedom such as spin, charge, and orbital. The interaction between them lead to many emergent properties and phases such as superconductivity, magnetism, and ferroelectricity as illustrated in Figure 2.1.

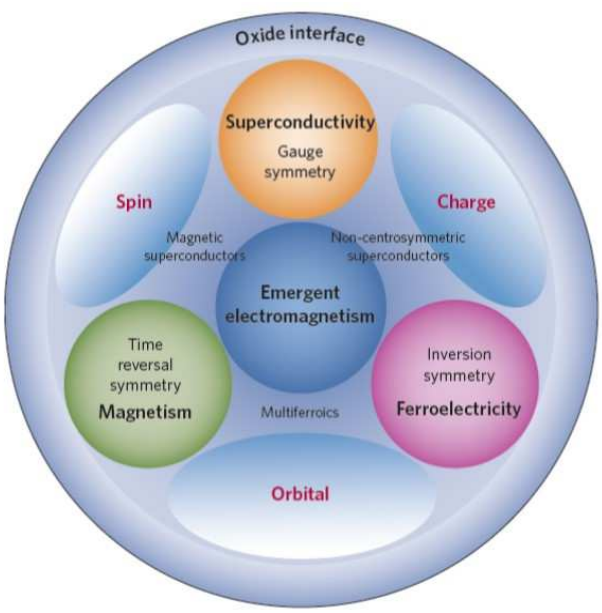

Figure. 2.1: Emergent phenomena at interfaces of oxide heterostructures due to interplay between charge, spin, and orbital degrees of freedom and dictated by various symmetries. Figure adapted from Ref. [11]

Because the scope of epitaxially grown materials is very broad, the report is organized into sections corresponding to several representative material classes

including nanowires, quantum dots, group III-Nitride, group III-Antimony, epitaxial spintronic materials, and oxides. Each class of materials has seen impressive progress often enabled by growth on high quality or foreign substrates, new methods for controlling doping and reducing defects density, and in-situ characterization techniques.

The common challenges for epitaxially grown materials include inadequate control of the interface properties, surface passivation, alloy composition, and growth of dissimilar materials. The feedback loop between growth, characterization, and device fabrication is rather lengthy and time consuming. Many academic research groups have found it very challenging to find adequate financial support to maintain the molecular beam epitaxial growth facility and to retain qualified personnel within the funding structures in the U.S.

As a few selected examples, the following strategies were suggested to tackle these challenges. Developing in-situ characterization tools, especially those capable of interrogating 3D structures would help improving uniformity of large arrays of nanostructures. Similarly, incorporating in-situ processing steps will accelerate the cycle of growth-characterization-device. Developing patterned substrates using nanoimprint or extreme ultraviolet lithography may yield site controlled, large scale growth of nanostructures. Advancing digital-alloy methods via MBE may provide control over ternary and quaternary compounds.

The areas identified as particularly promising for near-future explorations include: (i) topological materials including those hosting Majorana fermions and hybrid materials integrating topological materials and superconductors; (ii) improving nanostructures for quantum information and quantum optics applications; (iii) micro- and nanoscale integration of materials for optical, electronic, and magnetic devices; (iv) exploring neuromorphic devices.

2.2 Van der Waals materials

Van der Waals materials refer to a class of materials with strong, covalent (or ionic) bonding within two-dimensional layers and weak, van der Waals force between the layers. Because of this anisotropic bonding, a number of methods (e.g. mechanical exfoliation, chemical vapor deposition, and molecular beam epitaxial) can be used to produce quantum confined materials in the ultimate thickness limit of one or a few unit cells. The properties in van der Waals materials have been shown to strongly depend on the layer thickness. In the limit of a single or a few layer thickness, it is possible tune material properties via doping, strain, dielectric screening, proximity effects, stacking order, and external stimuli such as fields and light. In particular, vertical heterostructures formed by stacking two or more different materials provide many opportunities to control local electronic band structure, new quantum degrees of freedom, and new phases.

There have been many exciting scientific discoveries in the past ten years in the field of vdW materials. Formation of graphene and hBN on metal foils, development of CVD growth of transition metal dichalcogenides (TMDs), and MBE growth of various 2D materials are examples of notable breakthroughs. Symmetry dependent properties and new quantum degrees of freedom have been explored in monolayer and few-layer TMDs. Unique optical properties of excitons (bound electron-hole pairs) have been investigated and explored for optical manipulation of the valley index. Quantum emitters due to localized excitons were discovered in vdW materials. Coupling between different layers either in homo- or hetero-bilayers is found to drastically change

the electronic and optical properties of these materials. For example, techniques with atomic scale resolution such scanning tunneling microscopy (STM) revealed the formation of in-plane superlattices known as Moiré patterns, which sensitively depend on local atomic registration controllable by the twisting angle between the layers as shown in Figure 2.2. Optical spectroscopy methods with micron scale resolution provide complementary information. For example, high spectral resolution Raman spectroscopy revealed low frequency phonon modes, categorized as in-plane shear modes and out-of-plane breathing modes. Many-body interactions and cooperative coupling between different degrees of freedom lead to new phases such as enhanced superconductivity with high Tc (e.g. in FeSe on $SrTiO_3$) or increased critical magnetic field (e.g. in ion-gated MoS_2) and light-driven charge density waves (e.g. in TaS_2).

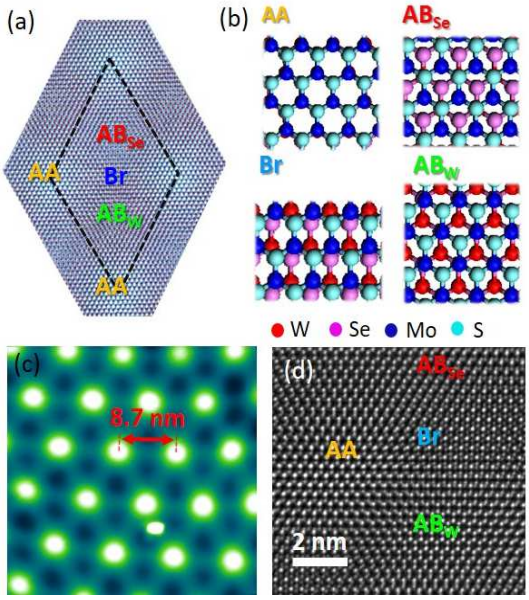

Figure 2.2: (a, c, d) calculated, STM, and TEM images of the Moiré pattern of rotationally aligned MoS2/WSe2 CVD grown bilayer. (b) illustration of atomic registration known as the AA, AB_{se}, bridge, and AB_w regions. Figure adapted from Ref [13].

Significant challenges remain in synthesis, characterization, and computation of vdW materials properties. While many scientific discoveries and prototypical devices have been made using monolayers and heterostructures created via mechanical exfoliation and stacking, far-fewer devices have been produced using epitaxially grown materials. Future technological development demands large area epitaxial growth, for which the availability of suitable substrates is a particular limitation. The extent to which properties of vdW materials can be controlled or modulated via external fields (electric and magnetic field) remains to be explored. It has been demonstrated that exciton and valley lifetimes are significantly extended in TMD heterostructures. However, their decoherence mechanisms remain to be investigated. While the Moiré patterns have been explicitly mapped out using STM with atomic resolution, their influence on transport and optical properties are not yet understood. To this end, characterization methods with improved spatial resolution are required. The interpretation of many experiments has benefited from DFT-based modeling. However, widely applied DFT methods still face challenges in accurately treating non-local effects and modeling large unit cells.

To make further progress, shared definitions of film quality for 2D materials are needed. In-situ characterization methods will provide information on domain size and orientation, and growth rate. To probe optical properties associated with the Moiré pattern in designer heterostructures, various scanning probe methods such as near-field scanning optical microscopy based on "Campanile" nano-probe, tip-enhanced Raman spectroscopy, tip-enhanced photoluminescence, and high resolution electron energy loss spectroscopy are all promising approaches. K-space probes such as nano-ARPES offer valuable complementary information. When combined with ultrafast lasers, ultrafast dynamics of carriers can be probed simultaneously.

Progress in vdW materials has been exceptionally rapid in recent years. It will likely maintain strong momentum in the near future, especially in the following areas. The development of hybrid MBE approaches that utilize precursors in place of evaporated metals and atomic layer deposition (ALD) techniques can provide a route to self-limiting growth. The precise assembly and control over twisting angle between atomically thin layers will open many exciting opportunities of quantum engineering in heterostructures. The interlayer excitons in heterostructures may permit long-range quantum coherence and formation of exciton or polariton condensates. Improved accuracy in experimental characterizations of properties of vdW materials and their heterostructures will motivate new computational methods that are capable of treating non-local interactions and exchange correlations. Exploring novel phases in monolayer and few-layer vdW materials subject to external stimuli by electric, magnetic, and optical fields will likely be fruitful endeavors.

2.3 Organic and flexible materials

The impact of electronic and photonic materials and devices on our daily lives could be broadened by circumventing limitations of more traditional materials imposed by size, weight, and compatibility with, e.g., the human body. The promise of organic and flexible materials, indeed, lays in the fact that they could enable a new generation of technologies including wearable or "imperceptible" electronics, large-area lighting, smart packaging products for food and drugs, and devices for human/machine interfaces, to name a few examples. This wide range of applications is underpinned by the development of a plethora of new materials targeted for specific functions. However, the lack of detailed understanding of fundamental` processes such as the multifaceted charge transport mechanisms (electronic-, ionic-, mixed conduction), the complex photophysical phenomena, the rich interfacial phenomena and, generally, the intricate processing/structure/ property interrelations in organic/flexible materials still poses significant intellectual challenges.

Despite these challenges, there have been many exciting developments in the field of organic and flexible materials in recent years. The fundamental understanding of the electronic and optical landscape of these class of materials, e.g., the energy loss mechanisms limiting organic solar cells, or the role of energetics of disorder in limiting charge-carrier mobility has drastically improved. This has led to the rational design of π-conjugated semi-conducting 'plastics' that exhibit field-effect transistor mobilities exceeding 10 $cm^2/V\cdot s$. This is sufficient for the fabrication of certain low-level digital transistor-based logic circuits. Further progress can be foreseen by the fact that a variety of promising n-type dopants have now been advanced, while only p-dopants had been available only a few years

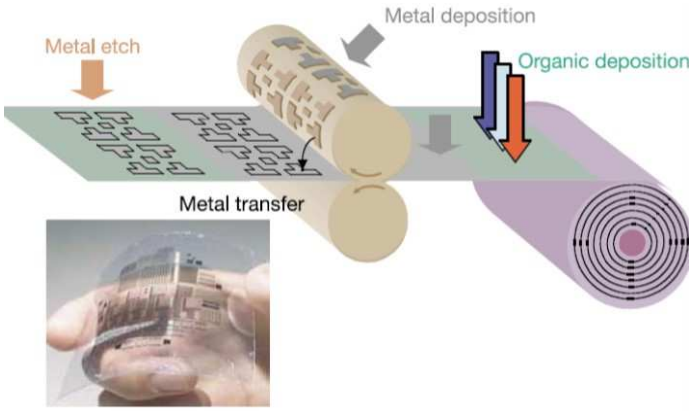

Figure 2.3: an illustration of organic device patterning process. On top of a plastic substrate, an organic and a metal strike layer are posited. After passing through two rollers with embossed patterns, the desired devices can be patterned using either a subtractive or an additive process. Figure adapted from Ref. [9]

ago. In the field of organic light-emitting diodes—another important device platform in the organic/flexible materials area—the use of "managers" to reduce triplet exciton-polaron annihilation reaction, has drastically improved organic LEDs' lifetime. As importantly as this progress in device design and fabrication, new tools for controlled deposition onto desired substrates now permit fine-tuning of structural features of organic/flexible materials platforms on the nano- to micron scales; they also frequently permit the creation of complex architectures on unusual substrates and carrier materials such as stretchable and deformable substrates (Figure 2.3). This has led, among other things to impressive progress in the bioelectronics field, most prominently in the area of skin wearable electronics and medical sensing applications. The advance in characterization tools, e.g. various X-ray techniques, have assisted the general progress in the field, both fundamentally and technologically, for instance, via in-situ analyses of thin films and more complex structures. On the theory front, the development of robust range-corrected functionals including dispersion terms, new methods of addressing the coupling between electron excitations and intra-/inter-molecular vibrations, the combination of molecular-scale electronic-structure calculations with nano-/meso-scale molecular dynamics simulations, the possibility of describing quantum coherent effects have all promoted improved understanding, and has contributed to the observed technological and scientific step changes.

Key challenges when working with organic/flexible materials originate from the varying degrees of structural and electronic disorder these materials systems often exhibit, rendering structural analysis is difficult because this low molecular order can lead to low signal. In addition, complex phenomena can occur at relevant interfaces and/or in heterostructures – an issue that is aggravated by the nearly infinite library of materials and materials combinations that exists and renders materials selection a most challenging task. For the technological advancement of this interesting materials class, achieving more versatile and stable n-doping, low cost manufacturing, high precision patterning over large area, stability and long-lifetime remain important challenges.

The inherent interdisciplinary nature of the field of organic/flexible electronics means that combined insights from chemistry, material science, physics, electrical engineering, and biology is necessary to address these challenges. Some of the much sought-after understanding may be derived from high performance computational methods combined with the most sophisticated characterization tools. The development of low-dose imaging, reconstruction methods, and cryo-electron microscopy may offer complementary opportunities to gain more structure information critical for working with organic/flexible materials with inevitable disorder.

Future opportunities are abundant: from highly emissive materials, true "synthetic metals" realized via doping, to new architectures based on multi-component, multi-phase systems, inorganic/organic heterostructures, stretchable materials, or objects with reversible functions. These could open new opportunities towards high current electronics, new photonic- and quantum information systems, and low-thermal budget devices. Long-lifetime, 100% internally efficient blue phosphorescent OLED will bring high commercial values. Thermoelectrics and radiation-hard matter are also of great interest. Organics and flexible materials ultimately promise "materials on demand" if fundamental challenges mentioned above can be addressed. Advances in innovative fabrications process, from printing, coating to additive manufacturing, have clear potential for enabling usch new technologies, including hydrogel-based electronics and other bio-integrated devices.

2.4 Metamaterials

The Greek word "meta" means "beyond". The field of metamaterials aims to design and synthesize materials with exotic properties that simply do not exist in naturally occurring materials by introducing artificial unit cells or inclusions. The most distinctive properties of metamaterials are defined by such artificial unit cells rather than the atomic unit cells. The field has been driven by the rapid development in computational power, nano-fabrication techniques, and characterization tools in the last two decades.

While early accomplishments were driven by engineering of constitutive parameters (e.g. permittivity and permeability) of component materials, the most recent breakthroughs in metamaterials have come from combing different degrees of freedom (e.g. via optomechanical and acoustoelectrical phenomena), developing new self-assembly approaches, expanding the frequency range of operations (e.g., U.V. and near- to mid-infrared), integrating metamaterial design with quantum materials, and achieving extreme-parameters (e.g. index near zero and large nonlinear susceptibility).

The key challenges that have prevented a broad range of applications of metamaterials can be summarized as limitations in loss, scale, scalability, and bandwidth. The loss of noble metals in the visible or of oxides in the near- to mid-infrared is too large to realize some metamaterial designs. The requirement to create sub-wavelength inclusions makes fabrication of metamaterials operating in the short wavelength range challenging. Fabrication methods can be divided to "top-down" and "bottom-up" approaches. While "top-down" approaches based on advanced tools such as e-beam lithography provide excellent control of ~ 50 nm or larger dimensions, these fabrication methods are not only expensive and time-consuming but also face serious challenges reaching smaller length scales or realizing 3D structures despite of some impressive proof-of-principle demonstrations as shown in Figure 2.4. It is worth noting that laser writing can produce 3D structures with dimensions comparable to the laser wavelength. In addition, many metamaterial designs are fundamentally limited to a narrow spectral range even in ideal situations.

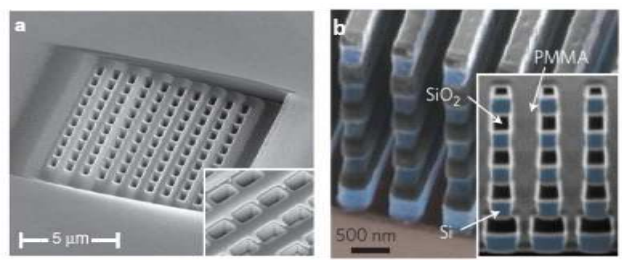

Figure 2.4: SEM images of (a) a 3D negative refractive index material and (b) a 3D near zero index metamaterial. Images adapted from Ref [10].

Much of the promise of metamaterials can be fulfilled by further reducing the dimensions of the artificial unit cells and by developing scalable synthesis methods. Self-assembly offers clear advantages in scale and scalability. Small nano inclusions with dimensions of ~ 3-5 nm can be produced rapidly and in large quantities. Nanocrystal assembly is typically driven by entropy and yields close-packed arrangement. Development of synthesis methods producing open and arbitrary architectures will open many new possibilities. Simulations and theory capable of incorporating quantum properties of active inclusion are necessary to accelerate the quantum leap of metamaterial designs.

Several research areas have been identified as particularly promising for future exploration. Experimental realizations of multilayer- or multi-component metamaterials will bring many opportunities. Dynamically reconfigurable metamaterials based on phase changing materials, liquid crystals, carrier injection, mechanical actuation, and nonlinearity will drastically expand the operation bandwidth. Both spatial and temporal modulations of material properties introduce new properties. Increasing the depth or contrast of modulations can be the key enabling element. The analogy of electronics and photonics lends to the concept of "optical metatronics", which may be further explored. Low energy information processing based on metamaterials points to a new route for parallel processing when integrated with traditional information processing devices.

2.5 Partnerships and National Initiatives

The industry representatives at the workshop are partners or members of the semiconductor research consortium (SRC), an organization that has provided a successful platform for public-private research collaborations for 35 years. Other industrial partnerships include the Flexible Hybrid Electronics Manufacturing Innovation Institute (NextFlex) and those with GlaskoSmithKline and Google. The signature programs supported by SRC (Nanoelectronics Research Initiative (NRI), Global Research Collaboration (GRC), and Semiconductor Technology Advanced Research Network (STARnet)) have all dedicated significant resources to materials research and achieved important breakthroughs in epitaxially grown materials and vdW materials. Particularly, SRC researchers have developed a comprehensive materials benchmarking database with a collection of reported material parameters, processing methods, and key properties for device applications.

For a novel material to be transitioned to applications in industry, both intrinsic properties and extrinsic factors (e.g. defects, parasitic, and contacts) are important. In addition, scalable manufacturing, e.g. wafer-scale material preparation and processing methods capable of producing high quality materials, is critical to bringing new materials from lab to fab. New materials that are compatible with standard materials used in CMOS devices and architectures likely have some advantages in being adopted by electronic industries. The development of new materials (e.g. vdW materials) and concepts (e.g., metamaterials) may take into account these criteria for industrial applications. To achieve these goals, material benchmarking should be developed and adopted by both academic and industry researchers.

Developing partnerships between the NSF-EPM program and industrial and national laboratory partners and cultivating cross-cutting collaborations with other national initiatives, are strongly recommended. Driven by the challenges at the end of CMOS scaling, industry is eager to explore basic research of novel materials. National laboratories in the U.S. support many unique and advanced computation, synthesis, characterization tools and a wide range of expertise relevant for EPM programs. Nanoscale Science Research Centers supported by DoE and Neutron scattering facilities supported by DoE and NIST are outstanding examples. Such programs aim to cultivate and support collaborations with academic researchers, and they have the potential to catalyze breakthroughs.

Among national initiatives and 10 Big Ideas for Future NSF Investments, quantum technology and quantum information are closely related to the research activities supported by NSF-EPM. All four working groups can readily identify their connections to "quantum leap" via developing materials

platforms for emergent correlated phases, new topological orders, single photon emitters, entangled photon sources, and photonic structures for quantum interconnects, to name just a few examples. The Materials Genome Initiative (MGI) combined with initiatives on "big data" science can clearly accelerate material discoveries via collaborative effort between computation, synthesis, and characterization. The National Strategic Computing Initiative's stated objectives include "establish a viable path forward in the "post-Moore's Law" era. Developing new materials is a key enabling element in searching for transformative technologies. While the Brain initiative does not focus on material science, bio-integrated electronics based on flexible and organic materials can contribute by "advancing innovative neurotechnology". Some outcomes of the Brain initiative, such as brain-like computing, can be applied to accelerate material discovery.

3. Epitaxially Grown Materials

3.1 Introduction

Epitaxial materials have had and are having a dramatic influence in broad areas ranging from condensed matter and optical physics, device engineering to modern commercial products. They have resulted in six Nobel prizes in physics with dramatic and long-lasting societal impact as the foundation for today's smart lighting initiatives, self-driving cars, fiber optic communication, medical diagnostics and cell phones.

In the past decade, epitaxial methods have been applied to materials from across the periodic table enabling next generation devices and systems through nano- and meso-scopic design directly connecting quantum mechanics and engineering functions. Compelling opportunities often arise because the interface between materials *is* the device. Current epitaxial research focuses on heterojunctions and the integration of dissimilar materials to create new functions. Promise of epitaxy lies in atomic control in all dimensions to design materials and artificial structures that cannot otherwise be created.

In the following pages, we summarize in-depth panel discussions on the "frontier of epitaxial materials". Panel members come from very diverse backgrounds and material emphasis from academic, national laboratory and industrial perspectives. We have structured this report covering the topical areas of nanowires, quantum dots, III-Nitrides, III-Antimonides, spintronic materials and epitaxial oxides. Below we summarize our common challenges, opportunity and impact areas along with suggested approaches for NSF to best support and benefit from this class of materials. Brief reports are also included on the benefits and challenges for each topical area.

The common challenges are to understand and control atomic details of more complex materials, thus to expand the tool kit by building on more traditional methods. As mentioned above, many modern devices and certainly the more innovative devices will depend on surface effects, thus understanding and characterization of chemistry and bonding at interfaces is crucial. Subtopics associated with interfaces include surface and interface state passivation, strain at interfaces between highly mismatch materials, epitaxy of dissimilar materials (e.g., metals and semiconductors or oxides and semiconductors), self-assembly, novel substrates, and selective epitaxy methods. These topics are strongly linked with modeling of growth mechanisms and precursor options. We note that materials characterization at the nanoscale and atomic scale is needed, especially for material composition and phase stability. Simultaneous development of

more complex theoretical models is needed to both interpret such characterization and to guide epitaxial research through an exponentially increasing parameter space. Thus, there is a strong natural overlap between the field of modern epitaxy and the Materials Genome Initiative.

We also discussed the common opportunities and anticipated impacts of epitaxial materials. As a baseline, epitaxy can drive applications for new phenomena providing atomic layer control, stability, uniformity, and a path to integration to systems for scale-up. The following topics in particular are ripe for significant advancement in the next decade:

•Topological materials

•Quantum information/quantum optics

•Neuromorphic devices

•Micro- and nanoscale integration of optical, electronic and magnetic devices

The first two of these have obvious connection to the Quantum Technology Initiative. Neuromorphic devices have the potential to mimic brain function and thus provide new insights relevant to the Brain Initiative. In the final area, microscale, massively integrated, multifunctional devices could also provide new tools such as tiny optogenetic probes or electromagnetic field sensors for monitoring nerve and brain function with minimal invasiveness.

Continuing the impact of epitaxial materials from basic physics to frontiers of new system applications, the common critical needs of this community include baseline support to upgrade, operate and maintain expensive infrastructure, an existential issue for epitaxy. Most countries leading in science and research have mechanisms to provide a baseline of financial support to their epitaxy infrastructure both at the institutional (through universities) and national (through Foundations) levels. With rapid expansion in Asia and Europe in both infrastructure and support, the lack of such mechanisms in the US has become alarmingly noticeable and increasingly so in future years.

•Stability of existing facility and infrastructure

It may be beneficial to have special grants that aim specifically at maintain existing growth facilities. At the university level, such facilities are typically established either through start-up funds or through the NSF MRI or DOD DURIP Programs. Following initial investment, there is no easy mechanism to maintain such infrastructure. As the size of a typical grant has not changed significantly over several decades, the portion of the funding devoted to maintenance has been steadily eroding. As a result, there is no mechanism to support a commercially built growth reactor through a single grant. We suggest developing a two-tier system of maintenance grants for small and large growth facilities, with the money earmarked to system maintenance.

•Growth and characterization

Many modern materials characterization techniques are very costly, and exist only at a few universities or specialized facilities, which have their own internal proposal systems (like many Light Sources and Neutron Facilities). In many cases, the most interesting physics occurs in – situ, and it is difficult to "bring" that stage of growth to a characterization facility. It may be useful to have a special program to support design and fabrication of growth chambers on existing beam lines, etc.

•Multidiscipline – modeling, characterization, devices

Programs such as DMREF are most welcome. In addition. small (2-3 PIs) collaborative teams could be supported to promote close collaboration between materials growth, theory, characterization and applications, while maintaining the agility and low overhead of a small effort.

3.2. III-V Nanowires

3.2.1. Promise and Benefit

Epitaxial growth of III-V and III-N nanostructures offers new functionalities to the fields of nanotechnology and solid-state physics. Several unique properties include but not limited to:

(1) 3-D geometries in nanoscale enable exploiting novel quantum physics and developing advanced device performances based on nanoplasmonics, nanophotonics, and nanoelectronics.

(2) nanoscale optical/electrical devices can be driven at ultra-low power, which is suitable for emerging system platforms requiring low power dissipation.

(3) elastic deformations can occur at heterogeneous interfaces, allowing growth of heterostructures with large lattice mismatch

(4) compared with thin-film heteroepitaxy, bottom-up growth of nanostructures provides a simpler and more flexible approach for large-scale hybrid integration, bringing great opportunity for commercialization.

3.2.2. Recent breakthroughs in Epitaxy, Characterization and Devices:

Epitaxy: Important advances have been reported which indicate the technological utility for nanostructure/nanowire especially associated with epitaxy. These reports are related to integration on silicon platforms for growth of uniform and high-quality binary/ternary nanowires on Si[21, 22] (Figure 3.1) which may prove compatible with heterogeneous integration on CMOS platforms. Also significant is the placement of QWs/QDs in nanowires with progress as indicated by position-controlled quantized structures with strong electron coupling[23, 24], novel geometries to include 2-D and 3-D nanostructures and unique branched/kinked nanowires[25], nanomembranes[26], and nanosheets[27]. Towards the realisation of devices, researchers have reported progress in surface passivation which demonstrate long carrier lifetime achieved by in-situ passivation by lattice-match III-V materials[28] or dielectric passivation layers[29, 30].

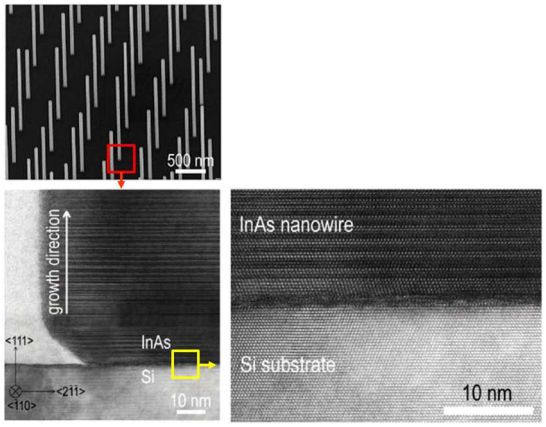

Figure 3.1: Fig. SEM image of InAs nanowires grown on silicon (upper), and cross-sectional TEM images showing the interface between InAs and silicon (lower).[17]

Characterization: Reported advances in characterization techniques include real-time imaging of nanowire growth by in-situ TEM to study adatom incorporation [31]; electron holography for electrostatic potential mapping[32]; measurement of material properties by resonant Raman

spectroscopy[33] and THz spectroscopy[34]; high-contrast nanoscale probing by femtosecond near-field[35]; 3-D in-situ photocurrent mapping by two-photon optical beam induced current[36].

Devices: Recent device demonstration in nanophotonics/nanoelectronics include single nanowire lasers at subwavelength scale in visible[37] and near-IR regimes[38]; III-V and III-N nanowire arrays forming random cavities[39] or photonic crystal cavities to achieve low-threshold lasing[40]; integration of telecom-wavelength nanolasers onto Si photonic platforms[41]. Detector especially avalanche photodiodes at near-IR with low dark current[42] have been reported.

High-efficiency core-shell nanowire solar cells have been demonstrated by selective-area epitaxy[43]; over 10% efficiency single nanowire solar cells on Si[44]; dual-junction solar cells on Si[45]. In the THz regime, single nanowire photoconductive THz detectors[46]; nanowire array THz emitters[47] were reported. In electronic devices, gate-all-around vertical III-V nanowire FETs/tunnel FETs on Si with low subthreshold slope and large on/off ratio, offering an alternative approach to replace and scale down current state-of-the-art 3-D FinFETs[48, 49].

Quantum technology: Regarding quantum technology, there have been several promising demonstrations to include nanowire single photon emitters on Si with embedded QDs, which can be potentially implemented in Si-based photonic integrated circuits[50]; InAs quantum dots in state-of-the-art low volume, high Q microcavities, bright emission of indistinguishability photons (single or entangled) have also been observed[51-53].

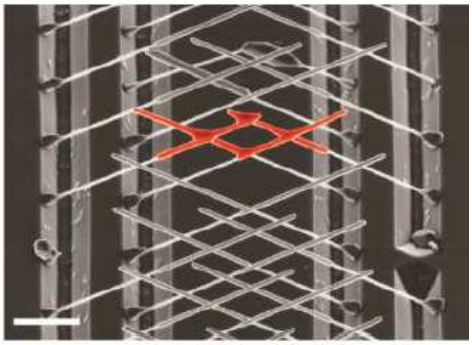

Figure 3.2. InSb nanowire networks as a platform for low-dimensional quantum devices[1].

Single photon avalanche detectors (SPADs) using InGaAs nanowires were reported at 1064 nm operating in free running mode with extremely low dark count rate[54]. Intersubband absorption in infrared regime by self-assembled quantized GaN/AlN nanowire heterostructures[55] were reported.

Quantum transport demonstrations include observation of Majorana fermions using InSb nanowire-based networks (Figure 3.2) and platforms[56]; quantized conductance at quantum point contacts in InSb nanosails – potential systems for spin-orbit quantum physics applications[57].

III-N: GaN and related alloys readily form stable nanowire structures that increase device architecture options. Many of the breakthroughs in III-N device technology have occurred through molecular beam epitaxial growth of AlGaN nanowires[24, 25, 58], which can be doped p-type more easily due to lower formation energy for Mg incorporation near growing surfaces[59].

3.2.3. Challenges and bottlenecks

Understanding growth modes and controlling nanowire properties: Due to the intrinsic 3-D geometries of nanostructures, the thermodynamics during growth is much more complicated than thin film epitaxy, and thus it is impractical to apply the same thermodynamics model of thin film to nanostructures. To date, it is still challenging to control crystal phase, i.e. zinc-blende or wurtzite, as well as planar defects (stacking disorders), especially in catalyst-free and self-

catalyzed growths. Thus, intensive fundamental studies are required to understand growth dynamics by both theoretical and experimental work. Also, the traditional characterization techniques, such as four-point probe, Raman spectroscopy, and X-ray diffraction, cannot be directly implemented in measuring 3-D nanostructures. As a result, the material study requires more costly/complex measurement approaches.

Optimizing device performance: Due to leakage current on large surface area, most of nanowire devices can only operate at cryogenic temperatures. Therefore, surface passivation needs further optimization to reduce leakage current by either in-situ passivation or ex-situ processes. Mechanical robustness and thermal stability of nanoscale devices also hamper their reliability, which require extensive studies on heat management and novel device processing techniques.

Meeting industrial standards for mass production: Several challenges have to be overcome for mass production. First, large-area growth of nanostructures encounters issues with reproducibility, uniformity, and durability. The surface quality also tends to degrade depending on the surface passivation. Second, templates for nanostructure growth are normally prepared by electron-beam lithography, which is not suitable for cost-efficient and high-volume manufacturing. As an alternative, nanoimprint or extreme ultraviolet lithography should be considered and developed. Third, most of high-performance devices are based on single nanowires, which are mechanically transferred onto foreign substrates after growth, resulting in more complicated fabrication processes.

3.2.4. Opportunities

Cross-linking with related areas will bring new opportunities. For example, there is an increasing effort on epitaxial growth of ultrathin van der Waals materials (e.g. graphene and TMDs). To date, epitaxial growth of these materials have not shown acceptable mobility for quantum structures. However, they are useful for detector applications. If the quality could improve, they would be very useful in quantum applications. Currently bulk material is grown and single layers are exfoliated following by a tedious device fabrication procedure. III-N nanostructures have some unique properties compared to their other III-V cousins that can be tapped. As selective epitaxy and controlled etching methods become more widely practiced, quantum structures with a high degree of size and location control have become available for the first time, including photonic crystal devices[60] and polariton devices.

3.3. III-V Quantum Dots

3.3.1. Promise and Benefit

Quantum dots (QDs) are zero dimensional structures exhibiting atomic-like density of states in contrast to solid-state structures of higher dimensions. Each QD still contains thousands to hundreds of thousands of atoms allowing for extremely large optical dipole moments. This explains excellent optical and electrical properties of QDs. Because of their localized structures, they are less sensitive to defects in surroundings than bulk materials and quantum well (QW) structures. Additional advantages of using QDs arise from their highly tunable properties that leads to a wide-range of applications. At present, the best candidate applications of QDs are quantum emitters, e.g., single and entangled-photon source[61], lasers[62], and detectors[63].

3.3.2 Recent breakthroughs

A major breakthrough of III-V InAs/GaAs QDs is the experimentally realized generation of high-performance quantum light sources, in particular single-photon sources. These sources will likely open up new avenues in quantum information and quantum optics[64]. Unfortunately, because of multiple levels of support, this development has occurred predominately in the EU (Germany, France, and the UK). Other quantum light sources include wavelength-tunable entangled photons, which will be used in quantum networks and quantum photonic circuits[61, 65]. Another breakthrough is the demonstration of the continuous-wave InAs/GaAs QDs lasers where the broad spectral gain leads to temperature insensitive devices. These QD lasers can be directly grown on silicon substrates with a low threshold current density of 62.5 A/cm^2 a room-temperature output power exceeding 105 mW, high operation temperature up to 120 °C, and a long extrapolated lifetime of over 100,158 hrs.[62, 66].

3.3.3 Challenges and bottlenecks

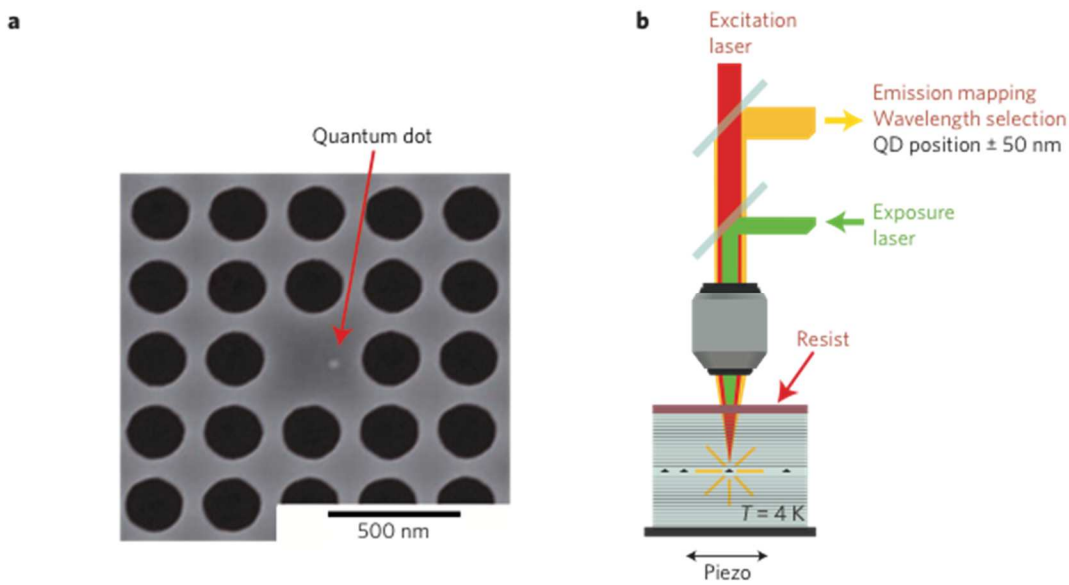

Figure 3.3: (a) Isolating a QD (marked) in the target defect mode of a photonic-crystal cavity (pcc)[18]. (b) Using an in-situ photolithography scheme yellow light (top) is used to image the QD state spectrally, while the green light is used to expose a photo-resist to define a device around the QD.

The main challenge in epitaxial QD technology results from the bottom-up self-assembly process used in their fabrication: QD placement is random with a large size distribution. The random arrangement of QDs in a device structure particularly hampers quantum emitter applications. Since only one QD is needed in a device, the random spatial distribution of QDs leads to many devices with too many or no QDs. One approach to address this challenge is to use in-situ photolithography, where a target QD state is first spectrally imaged, and then a green light source is used to define a device structure around the QD[66-69] (Figure 3.3). While highly-uniform self-assembled QDs have been obtained using several growth methods of migration enhanced epitaxy, droplet Epitaxy, and selective area growth[68], unexpected/unavoidable 'growth interruption', 'III-

V ratio', and 'growth temperature' would affect the uniformity of those QDs. Another challenge of growing high quality QDs is the presence of defects[69-71] (e.g., threading dislocations, staking faults, point defects, etc.), which formed in QDs/matrix material systems related with their large lattice mismatch, thermal expansion coefficient mismatch, polar material growth on a non-polar substrate (e.g., InAs QDs on Si substrate) and poor thermal conductivity of ternary alloy buffer.

Increasing single state coherence times: Because of the superior optical and electrical properties of InAs and GaAs QDs they are the natural choices for atomic-like optical states and electrically gated QDs. Short spin and phonon dephasing have limited some applications. While applications requiring electrically gated QDs can be realized in the Si-Ge material system exhibiting long coherence time, this strategy is not applicable for light emitting applications because of the intrinsically poor light emitting efficiency of Si-Ge. Thus, strategies for controlling dephasing in InAs QDs need to be developed[72].

Quantum dots and nanostructures play a critical role in quantum photonics, providing non-classical light sources, quantum memory, interconnects including waveguides, beam splitters, and circulators; and detectors. Not surprisingly, there is no one material that is suitable for all or even most of these devices. Thus, in addition to optimizing important properties in an individual material system, the challenge of integrating of several materials into devices and systems either through multiple deposition steps in highly mismatched systems or pick-and-place bonding techniques should be addressed.

3.3.4. Opportunities

If QD light sources can be integrated into chip-scale devices, such devices will create new opportunities in quantum logic and quantum information processing. If the electron or hole ground-state spin lifetime can be extended, this will provide an internal quantum memory and will have a significant impact on a wide variety of quantum systems including quantum repeaters and quantum logic gates. If more complicated photon states such as cluster states[73] can be obtained from InAs QDs, it would lead to major impact on distributed quantum information systems. While substantial efforts are underway in Europe, particularly in Germany, UK, and France, activities in QD quantum photonics is lagging in the US.

3.4. Group III-Nitride Materials

3.4.1 Promise and Benefit

GaN and related AlGaN and InGaN alloys first became important when materials breakthroughs in the 1990's led to the first practical blue and white light-emitting diodes (LEDs). Recognized by the 2014 Nobel Prize in Physics, understanding how to reduce defect densities on lattice-mismatched substrates, achieve effective p-type doping for the first time, and control composition in InGaN epitaxial layers has revolutionized illumination and diode laser technology. AlGaN HEMTs based on polarization doping for high mobility and high breakdown voltage have become the standard device technology for high performance microwave and radio frequency amplifiers. More recently, GaN is being tapped for power switching devices based on its combination of high breakdown voltage and low on-resistance. This unique material system continues to advance in performance and flexibility. III-N nanostructures are an important subset of III-N epitaxy research and progress, as described in the previous section.

3.4.2. Recent Breakthroughs

As LED technology has matured, new breakthroughs have come in "the green gap", a spectral region where InGaN alloys perform poorly. Progress is being made through understanding loss mechanisms and developing non-polar substrate growth methods[74] and epitaxial tunnel junctions to allow more robust ohmic contact fabrication methods[75, 76]. Breakthroughs are also occurring in devices operating in the ultraviolet, with LEDs[76, 77] and lasers[78, 79] emitting in the 230 nm to 270 nm spectral band. For planar films, the demonstration of degenerate p-type doping in GaN films with migration-enhanced epitaxy[80] identifies a new path to higher efficiency devices. The last few years have also seen the development of GaN vertical cavity surface emitting lasers (VCSELs), which require epitaxial growth methods for adding dielectric reflectors using flip chip technology[81] or epitaxially grown AlGaN/AlN Bragg reflector stacks.[82]

Power electronics applications of GaN are growing rapidly due to recent advances in vertical device designs dependent on p-n junction formation and regrowth in GaN to achieve breakdown voltages greater than 1 kV[83](see Fig. 3.4). Research on N-polar growth, previously avoided due to morphological difficulties, is now being pursued as a vehicle for increasing breakdown voltages in power diodes as well[84]. An important recent development in GaN epitaxy has been the successful demonstration of GaN-on-silicon epitaxy[85] to enable more cost-effective manufacturing due to both intrinsic material costs and the ability to work with large diameter substrates.

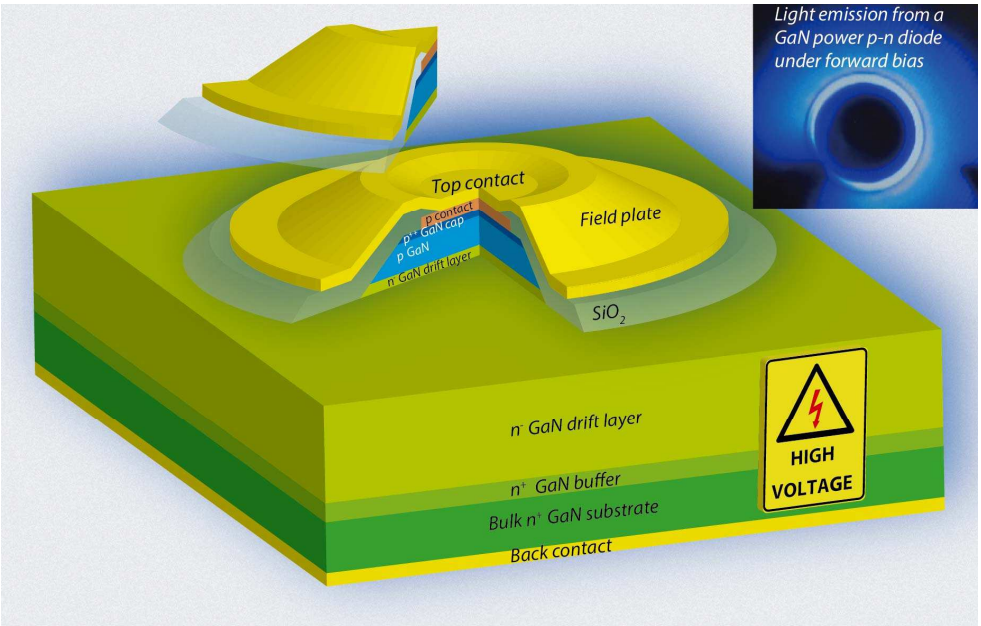

Figure 3.4: Schematic of a GaN power switch showing vertical design for high break-down voltage. [Unpublished, courtesy H. Xing and D. Jena, Cornell University].

3.4.3. Challenges

GaN epitaxial growth still presents challenges that have only been partly overcome to date. P-type doping remains difficult due to the high activation energy for the only viable p-type dopant, Mg, creating the need for relatively high dopant flux and atomic concentrations that in turn promote

defect formation and dopant diffusion. This problem is particularly acute for the ternary alloys AlGaN and InGaN. The nitrides are also less tolerant of wide ranges of V:III ratios, particularly in planar growth with molecular beam epitaxy, which limits one of the tools used by crystal growers to reduce defect formation and promote incorporation of dopants on the correct lattice site. Dopant diffusion and substrate quality are believed to be the primary limiting factors for progress in nitride power switching devices[86.]

In addition to direct growth challenges, growth methods are also being developed to mitigate processing challenges. For example, the poor performance of p-type contacting metallization schemes is one factor driving tunnel junction research so that devices containing p-type active regions are nevertheless fabricated with only n-type contacts[87]. The limited etching schemes available to fabrication of GaN devices are driving the inclusion of sacrificial epitaxial layers in devices for selective etching[83, 88].

The wurtzite crystal structure of GaN makes it the only common III-V semiconductor without cubic symmetry and therefore with polarity, and this factor brings both opportunities and challenges. The primary challenges are that polarity must be controlled during epitaxial growth and polarity inversion domains carefully monitored[89, 90]. This is particularly true for growth on silicon substrates. The various crystal faces of GaN present different growth rates and group III incorporation for ternaries. Subsequent crystal structure requires reoptimization of growth processes for different substrates and complicated 3D growth and regrowth designs[91, 92].

3.4.4. Opportunities

Research into measurement and control of ternary and quaternary alloy compositions in the AlGaInN alloy family will translate into devices with record efficiency because it will enable predictive designs that are not dominated by uncertainty and spatial inhomogeneity in alloy composition. Ideally this research would include computational methods for predicting crystal growth outcomes for strained layers, nanostructures and heterojunctions, in line with the vision of the Materials Genome initiative. New developments in atom probe tomography and scanning transmission electron microscopy, as well as more convention optical methods, are essential to such an effort. The effect of compositional fluctuations in InGaN[93] and AlGaN[94] on optoelectronic properties of quantum wells have already been shown to be significant through modeling and experiment.

Polarization doping combined with polarity control can also play a greater role in III-N device design. While the polarization-doped AlGaN HEMT is an established industrial product, exploitation of polarization to enhance p-type doping is still poorly understood. In addition, the established polarization constants for the nitrides have been reevaluated recently[95], leaving open the exploration of how established device design principles might be refined.

Significant advances are being made in bulk GaN crystal growth at companies such as Sumitomo, Mitsubishi, Sciocs, and Ammono. These substrates are now available on the general market and accessible to academic researchers, although quality and size remain less than ideal[96-98]. Research into the effect of substrate quality and alternative substrate schemes (such as growth on silicon) on device outcomes will continue to impact manufacturing for the foreseeable future.

Finally, group III nitrides combine the mechanical properties of a ceramic with the optoelectronic properties of a semiconductor. Thus, devices that exploit the unique mechanical properties of these materials are likely to grow in importance. Specific examples from the literature today include scanning probe tips[99] and resonator nanostructures[100, 101], but others remain to be invented.

3.5 Group III-Antimony Materials

3.5.1. Promise and Benefit

The III-Sb compound materials offer great flexibility in material and device engineering due to a wide range of infrared bandgaps, band offsets and electronic barriers along with high carrier mobility. The III-Sb material combinations and their related devices are highly promising candidates for numerous applications spanning from military to civil sectors, from electronic devices to near infrared (IR) laser sources to mid- and long-wave IR superlattice photodetector devices and focal plane arrays (FPAs). The unique transport properties and increase in the uses of IR photonics generated enormous interest over the last decade in III-Sb material fabrication as well as in III-Sb novel device development.

3.5.2. Recent Breakthroughs

Large-size GaSb substrate production: GaSb is the most popular substrate for III-Sb compound materials and devices. Nowadays GaSb substrates (2-inch, 3-inch, and 4-inch) via Czochralski technology have been available on the market. Most recently, IQE is able to supply GaSb substrates in large area (> 6-inch) for infrared imaging applications[102].

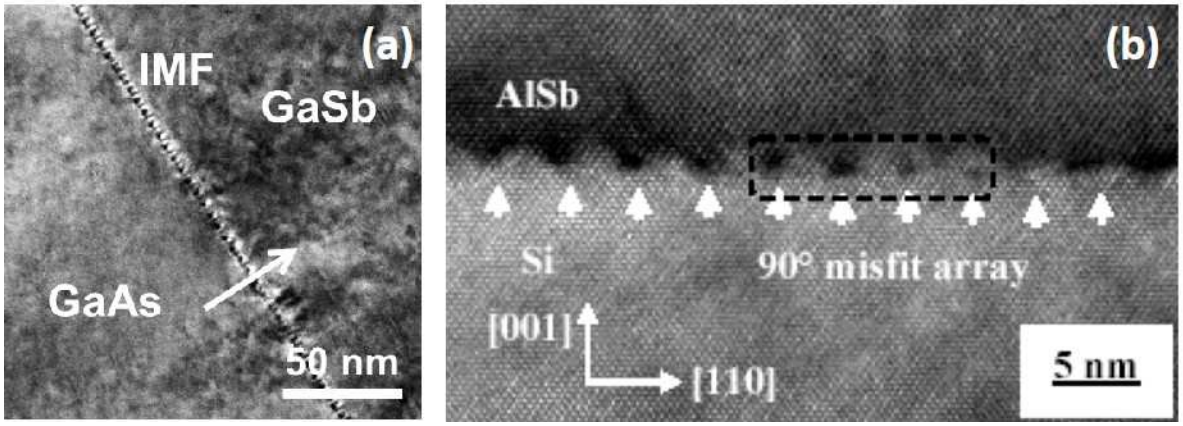

Figure 3.5: HRTEM image of (Left) GaSb grown on mismatched GaAs and (right) AlSb grown on Si substrate using IMF arrays.[2, 3]

III-Sb growth on foreign substrates: While recent technical advances have been achieved by III-Sb devices grown on native substrates, hetero-epitaxy on foreign substrates, such as GaAs, Si, and Ge are highly desirable for many applications (Figure 3.5). One popular research topic is developing the III-Sb based compound semiconductors on dissimilar substrates. The state-of-the-art methods to reduce threading dislocation (TD) density and improve the hetero-epitaxy layer quality include metamorphic buffer, interfacial misfit arrays (IMF), nucleation layer, TD filter layer, graded-composition ternary layer, use of mis-oriented/high-index substrates, or combinations of them. Via these methods, the TD density has been reduced 3-4 orders of magnitude to approximately $10^6/cm^2$. Some working devices (lasers, detectors, photovoltaic and thermophotovoltaic) based on III-Sb compounds on dissimilar substrate have been achieved. Most recent breakthroughs include: (1) III-Sb structure and emitters on Si using AlSb nucleation layer and GaSb/AlSb strain-relief superlattice[103, 104]; (2) GaSb growth on GaAs via IMF technology and thereafter III-Sb devices (solar cell, photodetector, TPV)[2, 105-107]; (3) High mobility InSb channels transistor using AlSb nucleation layer and growth of InAlSb metamorphic layers on GaAs and

GeOI[108].(4) High quality GaSb and InAs on pre-patterned Si substrates using high aspect ratio trapping[95].

Ternary and quaternary III-(As, Sb) alloys: Research on ternary/quaternary alloys offer more freedom on material/bandgap/property engineering in comparison with binary compounds. First, their bandgap energy and lattice parameter can be tuned independently by selecting the appropriate combination of group-III and group-V elements. Second, they are flexible to lattice-matched to InP, InAs or GaSb substrates. Third, ternary/quaternary III-Sb alloy combinations offer unique properties for opto-electronic devices. For example, they are especially attractive to the use of APDs with widely tunable bandgaps, low excess noise factor, high operation bandwidths. The III-(As, Sb) alloys have been reported to show the best excess noise factor for APDs, comparable to or below that of the mature Si devices[109-112]. Several research groups have been actively pursuing Sb-based ternary/quaternary alloy and related opto-electronic devices in recent years. More publications focus recently on the fabrication (random-/digital-alloys by both MBE and MOCVD), characterization (morphology, structural, optical, and carrier transport), and applications of ternary (InAsSb, GaAsSb, AlAsSb) and quaternary (InAlAsSb, AlGaAsSb) alloys[113-116].

Type-II superlattices (T2SL): Infrared detectors operating in the mid-wave (MWIR, 3-5 μm), long-wave (LWIR, 8-12μm), and very long-wave (VLWIR, >12 μm) windows are being developed. The T2SL materials offer unique optical and electronic properties, such as bandgap engineering flexibility, better uniformity (compared to HgCdTe), increased carrier lifetimes, suppressed Auger recombination, reduced tunneling currents, and normal incidence operation. The main materials used in T2SL include InAs/GaSb, InAs/InGaSb, InAs/InAsSb, and InAs/InGaSbN. The proposed T2SL structures include PIN, nBn, M-structure, W-structure, CBIRD structures. Current research focus includes barrier structure detector, Ga-free InAs/InAsSb detector, and multi-band detector. Although the advance in the past ten-years have significantly narrowed the material and device performance gap between T2SL and HgCdTe,[117-119] the remaining challenge is still how to improve the device performance to pass the MCT detector.

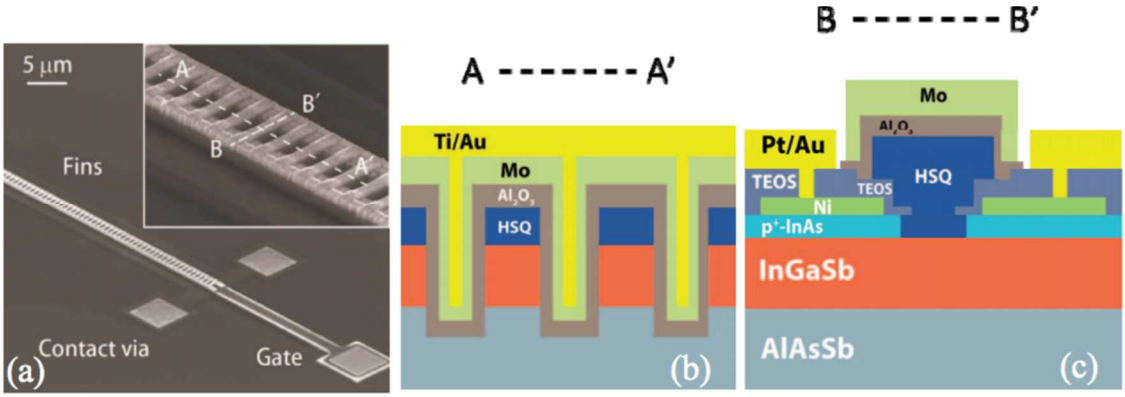

Figure 3.6: SEM image of an InGaSb FinFET before final pad deposition. [111]

Lasers and emitters: To date, the best QCL performance has been obtained by using different material systems, including AlSb/InAs grown on InAs, InGaAs/AlInAsSb and InGaAs/GaAsSb grown on InP substrates. Type-II In(Ga)Sb quantum-confined structures in InAs matrices offer a potential material system for inter-subband devices such as quantum cascade lasers (QCLs) or

interband cascade laser (ICL). Al(As)Sb material is commonly used as a suitable barrier material due to its very high conduction band offset. The use of different antimony-based heterostructures has led to laser emission operation above room temperature[120-122].

III-Sb electronics: III-Sb compound semiconductors have shown great potential to provide high-speed, low-noise, and low-power electronic devices (Figure 3.6) such as HEMTs, RTDs, and HBTs[123]. In addition, the high electron and hole mobilities of III-Sb alloys has gained great attentions with the potential to replace silicon in future CMOS technologies. With the application of compressive strain on InGaSb, the hole mobility has shown a strong enhancement via lowing the in-plane hole effective mass, resulting in a reduced power dissipation and increased operational speed for p-channel MOSFETs[124-126]. Another challenge limiting the transistor performance is the high-resistance source and drain contacts. Recently, this issue has been approached by using Ni-alloyed contacts, and showed a significantly reduced contact resistivity[127, 128].

Topological insulator: Following on the realization of topological insulating phase in HgTe/CdTe QW structures[129, 130], quantum spin Hall effect in InAs/GaSb QW structures has been proposed by Liu et al.[131] due to its unique broken band alignment. The experimental evidence of topological quantum phase transition taking place via helical edge mode has later been reported by Knez et al and thus attracted a great amount of interest in InAs/GaSb QW structures[132-137].

3.5.3. Challenges

One of the fundamental challenges is the ability to produce semi-insulating GaSb. The epitaxial GaSb usually presents a background doping level on the order of 10^{16} cm^{-3} regardless of current growth methods, suggesting a constraint to device design. For some applications, e.g. backside illumination sensors using III-Sb compound semiconductors, a semi-insulating GaSb substrate is highly desirable. However, semi-insulating GaSb substrates are hard to manufacture. Doped substrates give rise to inevitable free carrier absorption and degrade the photodetector response.

Eliminating surface leakage current in III-Sb devices is also challenging. The surface current is often limiting the attainable dark current, and becomes a significant issue to III-Sb opto-electronic devices, especially photodetectors. When exposed to ambient atmosphere, III-Sb will easily react with oxygen and form antimony oxide and elemental Sb. The semi-metallic nature of elemental Sb results in the conduction channel parallel to the semiconductor/air interface, leading to surface leakage current. As a result, proper surface treatments such as etching chemistry and passivation methods are of high importance to attain high performance III-Sb device and yet remain challenging.

For III-Sb epitaxy on foreign substrates, how to further reduce TD density remains challenging. Even though some studies have reported TD densities about 10^6 cm^{-2}, the vast majority of the III-Sb growth on foreign substrates still has TD density as high as 10^8 cm^{-2}.

The main challenge to develop high quality III-Sb ternary/quaternary materials is the spontaneous formation of clusters and phase separations during alloying, likely due to a very large and robust thermodynamic miscibility gap. This challenge can be partially overcome by the use of non-equilibrium technique such as MBE, which allows the growth in metastable and unstable regions. In order to fully overcome this challenge and further improve the material quality and

compositional uniformity, the state of the art includes ternary and quaternary III-Sb compounds by digital-alloy method via MBE[138-141]. This approach has been under active investigation, allowing greatly reduced growth fluctuation as well as phase separation for III-(As, Sb) alloys and enabling promising opto-electronic device performance.

3.5.4. Opportunities

The promising approaches to improve the TD density of III-Sb epitaxy on foreign substrates include development of new transition layer (Van der Waals bonding layer, graphene thin layer)[142], selective area growth (epitaxial lateral over-growth), and combination of TD reduction methods (metamorphic buffer, IMF, TD filter layer).

For topological insulators, compared to HgTe/CdTe, the unique InAs/GaSb QW structures offer advantages including tunable band structure via electrical fields and a good interface with superconductors[143, 144]. Thus, the InAs/GaSb system may can be suitable for the realization of TI/superconductor hybrid structures[145], which are predicted to host exotic Majorana fermion modes and can be used for topological quantum computation[146].

3.6. Epitaxial Spintronic Materials

3.6.1 Promise and Benefits

Epitaxial spintronic materials have made tremendous impact in the fields of memory technology (both magnetic disk and solid state) as well as condensed matter physics and may have a significant impact in Quantum Information Technology. The integration of magnetic materials with other electronic and optical materials has potential for developing low power spin based logic devices and devices with new functionality. Diluted magnetic semiconductors[147-149], which offer the potential of tuning magnetism through biasing[150], and magnetic insulators are offering additional new functionality. Integration with topological insulators[151] and Weyl semimetals may also offer new functionalities. Atomic defects (such as NV centers in diamond) are showing great promise for single electron spin manipulation with potential applications in quantum information technology at room temperature[152].

3.6.2 Recent Breakthroughs

Metallic Spintronics: The discovery of giant magneto resistance in epitaxial Fe/Cr superlattices[153] followed by the prediction of spin filtering properties of MgO in epitaxial Fe/MgO/Fe magnetic tunnel junctions[154-156] has led to amazing improvement in magnetic sensors (giant magnetoresistance (GMR) and magnetic tunnel junction (MTJ) based) used in magnetic hard disks and the development of MRAM technology. The development of CoFeB/MgO/CoFeB with perpendicular magnetization is now the material system of choice for MTJs[157, 158]. Spin transfer torque[159-161], Spin Torque Switching[162-164] and spin Hall switching[163] has led to the proposals for all spin-logic devices[165]. The efforts are now focusing towards perpendicular magnetic materials with even higher spin polarization for spin transfer torque switching MRAM (STT-MRAM). This potential application drives the development of half metals with 100% spin polarization. The prediction that a number of Heusler compounds are half-metals (100% spin polarization) has resulted in the development of Heusler based MTJs[166]. Some hexagonal Heusler compounds can also have perpendicular magnetization, but these compounds tend not to be half-metals. However, recent theoretical predictions suggest that some engineered cubic Heusler superlattices may have

perpendicular anisotropy and be half-metals[167]. Going beyond MTJ based memory, racetrack memory, which is based on current driven motion of domain walls[168] or Skyrmions[169], are promising for future technologies. Although most metallic spintronic devices utilize polycrystalline or textured materials, true epitaxial structures may lead to substantial improvement. The high performance CoFeB/MgO/CoFeB MTJs involve using MgO as a template for solid phase epitaxial growth of the CoFeB films, which are deposited amorphous and recrystallize by solid phase epitaxy on the MgO(001) tunnel barrier[170].

Heusler compounds: Heusler compounds can take on a vast variety of electronic and magnetic properties ranging from metallic, magnetic, including half metals, semiconducting, topological and superconducting[171]. A number of Heusler compounds have been grown epitaxially on III-V semiconductors[172, 173]. These have included ferromagnetic contact for spin injection[173-175], shape memory[176], semiconducting[177] and more recently, topological including a 3D topological material[178] and a predicted Weyl semimetal[179]. These all have potential for application in novel spintronic devices as well as devices for quantum information systems.

Semiconductor based Spintronics: The first definitive demonstrations of semiconductor spintronic devices based on spin injection from epitaxial ferromagnets (FM) were carried out a decade ago in GaAs[180] and Si[181]. Although the weak spin-orbit coupling in Si was an advantage in achieving extremely long spin drift lengths, particularly in vertical geometries[182], most of the important scientific and engineering problems in semiconductor spintronics have been addressed in epitaxial heterostructures based on III-V semiconductors. For example, the spin-dependent transport in epitaxial GaAs-based lateral spin valves operating at room temperature is now approximately the same as that achieved in the original devices operating at low temperatures a decade ago[175]. This progress has been enabled by several factors. First, spin injection ferromagnetic metals into semiconductors relies entirely on engineering of interfaces. Although the capabilities of MBE for the growth of high-quality semiconductor heterostructures are well-known, the most essential aspect in the case of spintronics has been "dissimilar materials epitaxy" of ferromagnetic metals on semiconductors. Progress in both growth and characterization of ferromagnetic metal (FM)/III-V interfaces has made this system the most reliable among the common platforms for semiconductor spintronics[183]. Second, the explosion of interest in advanced magnetic materials, including Heusler alloys, which can be grown epitaxially on the $In_xGa_{1-x}As$ family of semiconductors[173] (Figure 3.7), has provided a route to highly efficient spin transport devices with a wide range of magnetic properties, including perpendicular anisotropy. Third, recent progress has led to the achievement of spin injection and detection in FM/III-V heterostructures incorporating two-dimensional electron gases[184], which represents substantive progress towards a spin field-effect transistor, one of the long-standing goals of semiconductor spintronics. Finally,

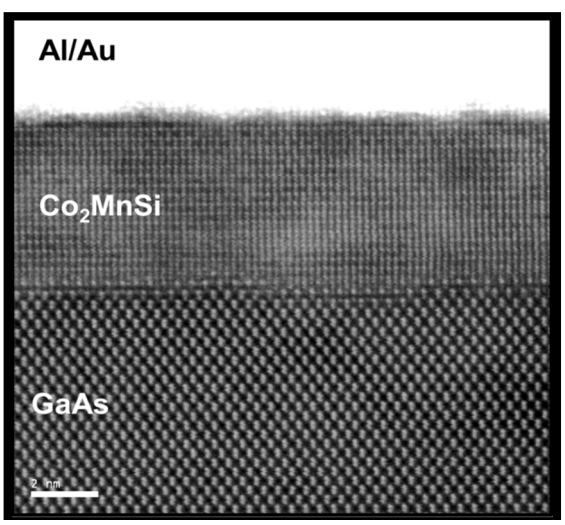

Figure 3.7: HAADF-STEM image of a Heusler/GaAs(001) epitaxial heterostructure.

advanced characterization techniques, including scanning transmission electron microscopy[185], are uniquely suited to the study of epitaxial heterostructures. These have not only provided a means of probing FM/semiconductor interfaces with atomic-scale resolution, but also a route for comparison between experiment and the predictions of electronic structure calculations.

Quantum Information: Replacing the ferromagnet contacts with superconductors on a semiconductor nanowire has been predicted to result in the formation of Majorana Fermions[186]. The first experimental indications[56], epitaxial Al on III-V semiconductor nanowires[187] and 2D films[188], have led to exciting new results in Majorana physics. Improvement in superconductor/semiconductor interface contact transparency has been made recently[189]. These recent results are showing great progress toward the realization of semiconductor based topological quantum computing.

Since the proposal of using semiconductor spin in quantum dots for quantum computation[190], there has been a strong emphasis for developing gate controlled semiconductor spin qubits. The growth of exceptionally high quality epitaxial heterostructures have been critical in developing gate controlled quantum dots in III-V[191] and Si/SiGe[192]. The suggestion of a nuclear-spin based quantum computer using phosphorous donors in Si[193] led to the development of epitaxial growth techniques combined with scanning probe microscopy to control the placement of phosphorous dopants with atomic precision[194]. The engineering and manipulating atomic-like spins in semiconductors has been coined 'Quantum Spintronics'[152]. Nitrogen-vacancy (NV) centers in diamond can be used for single electron spin detection[152]. Epitaxial growth of isotopic layer heterostructures and nitrogen doping control has been used to control the position of the NV centers[195]. Wide-band-gap nitrides are also likely to contain color centers that could be potential candidate for qubits[196].

3.6.3 Challenges and Bottlenecks:

Challenges: Major challenges involve continued support to be able to maintain and operate high quality epitaxial growth systems, such as MBE systems. High quality MBE semiconductor growth systems require dedicated people to ensure proper operation and maintenance to keep contamination down and material quality high. These systems require a continuous flow of liquid nitrogen coolant of several 100s of liters per day. High purity source materials are expensive and so are all components for the MBE systems. A catastrophic vacuum failure can result in >$100k of damage (an Sb cracker cell by itself is ~$100k). The typical NSF grant does not cover much more than one graduate student and a few supplies. It would not cover the operational cost of an MBE system. Hence, multiple grants and projects are needed in order to keep an MBE system operational.

Understanding how to control growth and interfaces between dissimilar materials is an outstanding challenge. Thermodynamics, differences in crystal symmetry and atomic bonding all affect the interface properties and defect formation. Epitaxial lattice mismatch is always a problem and new approaches for controlling or eliminating these inherent defects to minimize their impact on performance are needed.

The interface properties are becoming more important for device performance and often the dissimilar material heterostructures require fabrication without exposure to air. In order to minimize contamination of growth systems, multiple interconnected growth chambers for the different materials are needed. Furthermore, for some more complicated and novel device designs in-situ processing steps involving patterning and etching may be required. This would require major upgrades to typical epitaxial growth systems.

Bottlenecks: On the more fundamental side, the development of quantum information materials and systems based semiconductor heterostructures relies on continued improvements in materials properties and control down to the atomic level. The time for feedback between epitaxial growth and characterization can be very long (months to years) as often the critical characterization involves measurements at cryogenic temperatures (10s mK) such as magnetotransport measurements on completely fabricated devices. Measurements at liquid nitrogen or liquid helium temperatures are often not sufficient. To overcome the challenges of slow feedback, the materials synthesis teams will have to develop the ability to fabricate simple test structures and perform characterization measurements down to 10s mK temperatures. This requires additional resources in equipment and people.

3.6.4. Opportunities

In the last several years, the explosion of interest in topological insulators has been accompanied by a renewed focus on spintronics in materials systems with strong spin-orbit coupling. This development represents one of the most promising frontiers in III-V spintronics. There has, however, been remarkably little work on ferromagnet/semiconductor heterostructures in narrow-band III-V materials. New approaches to spin injection, including spin pumping[197], are uniquely suited to interfaces such as FM/InAs or FM/InSb in which a Schottky barrier is either absent or very small. In particular, spin pumping, along with detection by the inverse spin Hall effect, provides a promising route to circumventing the conductivity mismatch problem[198], which is now viewed very differently from it was a decade ago. This means that the capacity to exploit the strong SOC in InAs and InSb-based heterostructures now exists if interfaces suitable for spin-pumping can be prepared. At the same time, the ability to engineer layer by layer growth of Heusler compounds on III-V's has opened a route to controlling the magnetic anisotropy[167] and hence the orientation of electrically injected spins. The outstanding microwave properties of epitaxially grown Heusler alloys have played a critical role in new techniques for probing spin dynamics in FM/semiconductor heterostructures[199]. Finally, recent progress in the growth of high mobility 2DEGs in InAs-based heterostructures provides a path to two-dimensional devices with strong spin-orbit coupling[200]. Integrating such a device with, for example, a highly polarized Heusler compound spin injector and detector is conceivable if there is a sustained and coordinated effort in materials and device physics. Moreover, although it has never been fully exploited, the prospect for optical control and readout in the infrared provides the narrow-band III-V's with a capability that complements electrical injection and detection.

Clearly there are great opportunities for developing quantum information systems, new applications and also new discoveries based on semiconductor heterostructures, particularly as these are integrated with other materials such as superconductors. Using the ground-state spin manifold and an optical transition in the NV defect in diamond and now SiC, a very sensitive magnetometer has been made in diamond[201, 202]. This system can also be used to store single spins

for quantum memory, especially if spin transfer to a ^{13}C atom is used. Another emerging application is quantum sensing. An AFM incorporating an NV center[203] at the tip has been used for a single-spin quantum sensor for magnetic imaging[204].

3.7. Epitaxial Oxides

3.7.1. Promise and Benefits:

The epitaxial perovskites and transition metal oxides in general are currently enjoying a true renaissance. Novel deposition techniques such as oxide molecular beam epitaxy (MBE), pulsed layer deposition (PLD) and atomic layer deposition (ALD) have extended essentially atomic control to this class of materials. The ability to grow ultra-thin films and heterostructures, including those with quantum confinement, is enabling breakthroughs in fundamental physics and applications alike. This new physics can lead to potentially transformative applications such as high-k dielectrics[205-207], resistive switching memory[208, 209] and negative capacitance devices[210], two-dimensional electron gas (2DEG)[211, 212], superconductivity[213], metal-to-insulator transition[214, 215], quantum wells[216] and electro-optical effect-based devices[217, 218].

Perovskites and other transition metal oxides are unique, due to the presence of d-electrons of transition metal ions. The properties of these materials are controlled by a delicate interplay of the electrostatics (the crystal field splitting) and the Pauli principle (the exchange). These effects give rise to emergence of different kinds of order, for example ferromagnetism, superconductivity or ferroelectricity. This is a striking example of a direct relation between the fundamental physics and practical use. In the ions of the iron group, for example, the energy scales of both effects are rather similar making their respective oxides very sensitive to small variations in the environment (strain, doping, etc.). This in turn allows for their use in sensors and switches. Sensitivity of electronic and magnetic properties to stoichiometry enables applications in memory devices.

3.7.2. Breakthroughs: Almost 20 years ago, McKee showed the path to integrate the perovskite oxide $SrTiO_3$ on Si(001) by MBE[205]. This new process led to the integration of many oxides on many common semiconductors including Si, Ge, and GaAs[219]. This development occurred at roughly the same time with breakthroughs in oxide PLD[211] and ALD[220]. Also, new, faster MBE techniques have recently become available[221]. Integration of ferroelectrics and other ferroic materials on semiconductors opened up many exciting possibilities[222, 223] as did the discovery of a 2DEG at certain oxide interfaces in a new and growing field[224]. Perhaps most unusual is the recent discovery of polarization vortices in thin perovskite films[225]. All these advances became possible because of the development of high-pressure RHEED, oxygen-tolerant metal sources and substrate heaters. In particular, control of perovskite growth via RHEED (phase modulation of RHEED oscillations as well as surface termination control via appearance of higher order spots) was instrumental in achieving this atomic level control of epitaxial perovskite films and heterostructures.

3.7.3. Challenges: Oxide epitaxy has the potential to make a serious impact on many emerging technologies, but it still faces formidable challenges[226-231]. Among them are the relatively slow growth rate, high thermal budget needed, sub-unit cell control and the related issue of controlling dynamic layer rearrangement in pervoskite materials (e.g. TiO_2 plane swaps with SrO plane). Another major problem is the precise control of cation stoichiometry (sub-1%), and reduction of point defect concentrations to the level of semiconductor epitaxial layers. Overall, the film quality

routinely achieved is still not as good as that of a bulk substrate, and MBE-grown films suffer from severe oxygen deficiency.

In addition, there are University-specific non-scientific challenges in doing oxide and perhaps other kinds of epitaxy. Firstly, the cost of a modern growth reactor is over half a million dollars. If one adds the analytical equipment, the million-dollar threshold is crossed (one often ends up with a multimillion dollar investment). Raising the equipment money on that scale beyond the start-up, presents an obvious challenge. In addition, maintenance is on the order of 10% of the equipment cost, which immediately requires multiple federal grants to support a single growth reactor. The equipment is complex and its long-term usability is increased by having a permanent technician associated with it. There is no mechanism in a typical university in the U.S. to support such a position. It is worth pointing out that a state-of-the-art reactor is not really a user facility in the same sense as, e.g., a standalone SEM. It can only be a collaborative facility. In addition, though UHV equipment doesn't require a clean room, it does require infrastructure (chilled water, compressed air, high current, air conditioning and some air filtration to name a few). This makes epitaxial growth groups rare, and they typically are a part of a larger Center, where the cost can be distributed, which is a limiting factor from the scientific diversity and originality point of view.

3.7.4. Opportunities

Many exciting opportunities exists creating and exploiting artificial oxide heterostructures such as superlattices, quantum dots, etc. and in integrating oxides with other materials such as semiconductors, .e.g., Si, Ge, GaAs or GaN or two dimensional materials such as graphene, h-BN, or dichalcogenides of transition metals (WS_2, $MoSe_2$, etc.). The opportunities are both fundamental and applied. The ferroic order in transition metal oxides is sensitive to epitaxial strain and is affected through orbital selection by quantum confinement. Thus, the physics of oxide films and their interfaces in the 2D limit are found to be quite different. On the applied side, one can use oxide films either as elements of conventional devices, or in hybrid technologies. For example, the ionic motion and related memory effects can be used in so-called mem-computing, sub-threshold switching can be achieved in ferroelectric negative capacitance devices or metal-to-insulator transition devices. Their electro-optical properties may have a significant impact in Si photonics. Finally, a combination of the abovementioned approaches may have applications in neuromorphic computing.

4. Van der Waals Materials

Van der Waals (vdW) or "2D" materials are the focus of tremendous research efforts worldwide due to their broad range of distinctive physical properties that are uniquely enabling for current and future technologies. The Electronic and Photonic Materials (EPM) Program in the NSF Division of Materials Research plays a central role in supporting vdW materials research leading to discoveries of novel structure-property relationships that open up new avenues of fundamental inquiry and serve as the basis for engineering new technologies. Given the breathtaking pace and scope of exploration in this area, it is useful to review the status of vdW materials research and the identify priorities in the larger context of electronic and photonic materials.

Based on important breakthroughs and challenges in vdW materials identified by the workshop participants, the discussion was organized around unique characteristics and phenomena including (1) new concepts for electronic and optoelectronic devices based on couplings between internal

degrees of freedom such as "valleytronics"; (2) new electronic phases and new device behaviors arise from strong coupling to *external* fields in ultrathin vdW materials; and (3) new behaviors arising from coupling between vdW layers in "stacked" heterostructures. A distinctive physical characteristic of vdW materials is the combination of covalent or ionic in-plane bonding with van der Waals bonding between planes, which may enable exfoliation. Properties are typically layer dependent depending on the degree of interlayer interactions, and the stability varies widely[232], ranging from graphene at one extreme to phases that *may* require a substrate to stabilize. Materials that presently require substrates to stabilize were not discussed in detail as greater understanding is needed before developing applications. Solution processed materials such as inks, despite the early promise shown for applications, were also not discussed. Materials of particular interest include graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (TMDs), as representative (semi)metallic, insulating, and semiconducting systems.

In the following report, the workshop findings were organized into four topical themes: (1) Growth and processing of vdW materials; (2) Exploiting couplings derived from symmetry of monolayers; (3) Characterizing interlayer interactions; (4) New phases of 2D matter. Summaries of the discussions on these themes follow below. Within each topical theme, the report identifies recent breakthroughs, opportunities created by these breakthroughs, challenges and open questions to be addressed, and important future directions with transformative impacts. The participants identified additional cross-cutting topics of high interest, including mixed-dimensional heterostructures, hybrid interfaces for charge separation and doping, coupling to mechanical degrees of freedom including piezoelectricity, and applications in flexible electronics. As discussion time was limited, aspects of these research areas are highlighted as important new directions at the end of this report.

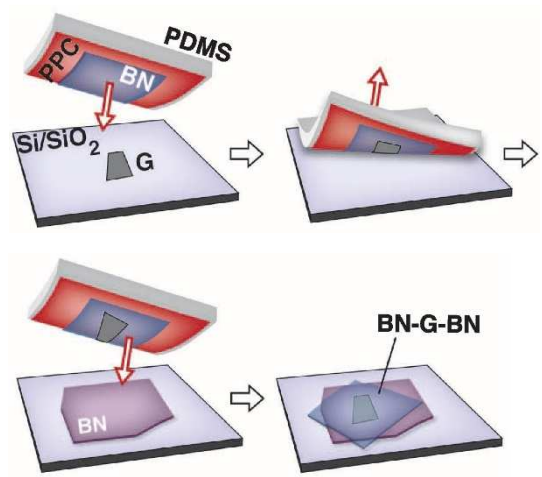

Figure 4.1. Fabrication of a stack of 2D materials using exfoliation and transfer.[12]

4.1 Growth and Processing of vdW Materials

A unique aspect of two-dimensional (2D) materials in comparison to conventional three-dimensional materials is that, in addition to epitaxial growth, the 2D materials can be prepared using exfoliation and transfer (Fig. 4.1). In these procedures, μm-sized flakes of 2D materials are separated from bulk crystals using adhesives, and such flakes are then transferred onto a desired substrate. (Larger areas of 2D materials can in some cases be prepared by separation from metal foils on which they are grown,[233, 234] although the quality of the material is generally not as high as for the flakes from bulk crystals.) Stacks of 2D materials, forming a heterostructure, can and have been constructed by exfoliation and transfer. [235, 236] Nevertheless, for wafer-scale production of devices based on 2D materials, it seems likely that epitaxial growth processes will be required. An important consideration regarding such growth is that 2D materials have an intrinsically weak bond between layers (i.e., only a van der Waals interaction), so that many of the traditional epitaxial

processes do not apply for 2D materials. Nevertheless, the term "van der Waals epitaxy" was coined many years ago,[237] and it is in this spirit that most of the present work (i.e., the portion of the work involving *additive* deposition) on epitaxy of 2D materials is performed.

Workshop participants discussed several breakthroughs in the field of epitaxial growth of 2D materials, including epitaxial formation of graphene on SiC (*subtractive* formation, in which Si atoms preferentially sublimate, leaving behind the C which self-assembles into graphene);[238,239] formation of graphene and h-BN on metal foils (by deposition and/or segregation);[240,241] use of h-BN as a substrate and/or capping layer (although applied primarily to date only for exfoliation/transfer processes);[242, 243] the development of chemical vapor deposition (CVD) methods for TMDs, using vaporization of powder sources and transport of the vapor by a carrier gas to the substrate;[244] use of suitable molecular precursors for gas source CVD processes, such as metal organic CVD (MOCVD); epitaxial deposition of TMD films on sapphire (Fig. 4.2);[245] and development of molecular beam epitaxy (MBE) methods for various 2D materials, including TMDs[246-248].

Despite the advances, large-area epitaxial growth of 2D materials is still at an early stage of development and many challenges remain. The availability of suitable substrates is a particular limitation. The substrate should have a small lattice mismatch (or a coincident site lattice) with the 2D material of interest to provide a template for epitaxy. Due to the sensitivity of 2D monolayers to their dielectric environment, the substrate should ideally be insulating and exhibit minimal potential fluctuations from surface roughness, steps or wrinkles. Suitable substrates must also be of a sufficiently large size and commercially available. C-plane sapphire meets many of these requirements and has been used for epitaxial growth of MoS_2 and WSe_2.[249,250] However, the surface step density is high and TMD domains can exhibit several different orientations on the sapphire surface[17], leading to anti-phase boundaries and other defects. The van der Waals surface of h-BN is therefore of interest for epitaxy. However, bulk h-BN crystals are limited in size and availability. Consequently, efforts have focused on growth on small area exfoliated h-BN flakes. Advances are therefore needed in bulk growth of h-BN and development of h-BN template layers of suitable quality for 2D epitaxy, as well as in the identification and development of other substrate materials for van der Waals epitaxy.

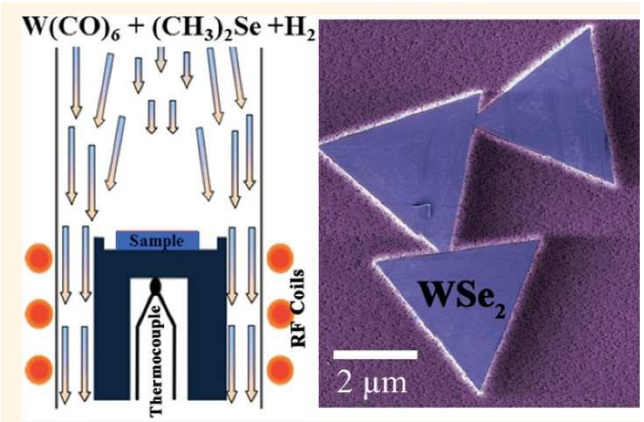

Figure 4.2. Illustration of MOCVD Growth of WSe_2 and the optical microscope images of the monolayers grown [15].

In addition to substrates, processing advances are needed to develop epitaxial growth technologies for layered chalcogenides and other 2D materials comparable to those that exist for III-Vs and related systems based on gas source CVD, molecular beam epitaxy or a hybrid of the two methods. In the area of gas source CVD, including MOCVD, high purity precursors are needed for a wide

range of 2D materials, as well as studies aimed at understanding the impact of precursor chemistry on impurity and point defect levels in the films and monolayer growth and properties. The development of hybrid MBE approaches that utilize precursors in place of evaporated metals and atomic layer deposition (ALD) techniques that provide a route to self-limiting growth at the monolayer level are also of high interest. Additionally, ALD techniques, which involve relatively low growth temperatures, are of significant interest for flexible electronics and integration with back-end-of-line processing in integrated circuits. A tight coupling of theory/simulation with growth experiments is needed to provide insights into the fundamental mechanisms controlling epitaxial growth.

Research programs (e.g., the NSF 2-DARE EFRI program) that include both materials and device development in a coupled feedback loop are powerful in addressing some of the above challenges. Advances in characterization are needed to provide more rapid feedback on epitaxial film quality including techniques to analyze film orientation, composition, layer stacking and analysis of defects such as grain boundaries, dislocations and point defects. The definition of film quality standards for monolayer TMDs and other 2D materials will facilitate comparison and benchmarking with single crystal bulk material. In-situ characterization methods are also needed to provide real time information on domain size, density, orientation and monolayer growth rate for both gas source CVD and MBE to provide further insights into the growth mechanism as well as improved process control.

Novel electronic and optical devices have been developed through the use of 2D materials obtained by exfoliation and transfer, thus providing proof of principle of such devices. However, far fewer such devices have been fabricated using material produced by epitaxial growth. For example, interlayer tunneling field-effect transistors have been successfully fabricated by exfoliation and transfer,[251-255] but the difficulty of both heteroepitaxy and integration of vacuum-deposited (as opposed to transferred) dielectric layers has limited the development of such devices using large-area processing methods.[255] Nevertheless, with continued development of such methods for 2D materials, there are great opportunities to impact the field of wafer-scale, novel electronic devices and circuits.

4.2 Exploiting couplings derived from symmetry of monolayers

Much of the recent progress in revealing unique properties of vdW materials exploit their layer dependent properties, in particular symmetry. One notable example is the valley dependent electronic and optical properties of TMDs (e.g., XM_2, X=Mo, W, and M=S, Se in the 2H structure). In monolayer TMDs, inversion symmetry breaking together with strong spin-orbit coupling in the metal *d*-orbitals leads to coupling between the spin and valley degrees of freedom, as illustrated by Fig. 4.3a. Valleys refer to band extrema in momentum space. In monolayer TMDs, there are two inequivalent, but energetically degenerate valleys, the K and K' points at the boundary of the Brillouin zone. Time-reversal symmetry dictates that the electron spins in the K and K' valleys have opposite signs leading to distinct optical selection rules for the two valleys (Fig. 4.3a) that allows access to a given valley with circularly polarized light. The valley index has been proposed as a new information carrier[256]. The valley pseudospin can be manipulated with a magnetic field[257, 258] or an off-resonant laser via the dynamic Stark effect [259-261], thus permitting rotation of the valley Bloch vector, as illustrated in Fig. 4.3b. [33]

Following the optical generation of valley polarization, the valley index can be further manipulated electrically and spatially separated via the valley Hall effect [262, 263]. The lifetime and dephasing time of the exciton, is rather short, around 1 ps or even faster. This limits the time scale over which optical manipulation can be implemented [264]. Trions, i.e., charged excitons, exhibit somewhat extended lifetimes and dark excitons may provide another route to longer retention of valley information. [265] In addition, valley information initially contained in excitons may be transferred to resident electrons and holes, which have been shown to exhibit long valley lifetimes, suggesting the possibility of long information storage time in valley index [266].

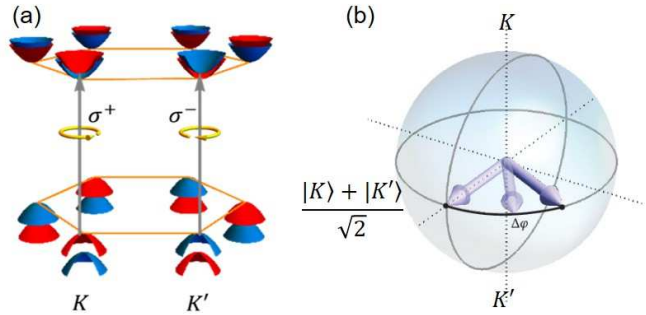

Figure 4.3 Electronic and valley properties of TMD monolayers. (a) Illustration of band structure near the K and K' valleys and spin-valley locking, with the red and blue colors corresponding to opposite spin. (b) Bloch vector representation of valley index and its optical manipulation.

In general, new quantum degrees of freedom, new phases, and the ease of controlling such properties via doping and strain create many opportunities to explore fundamental scientific questions and potential applications based on atomically thin materials. Compared to bulk materials, the thinness of van der Waals layers allows one to achieve unusually high doping densities by gating or photoexcitation. Similarly, strong tuning of the electronic structure and band gap can be achieved through the application of large achievable (and spatially controllable) strain fields. A method of tuning the properties of a 2D layer that does not have a direct analog for bulk materials is modification of a 2D material's electronic structure through its dielectric environment. For ultrathin layers, the surrounding media can significantly modify the many-body interactions within the material itself. This permits tuning of the band structure simply by altering the external dielectric environment, an approach termed "Coulomb engineering". [267]

Many open questions and challenges remain to be addressed via a collaborative effort among researchers working on synthesis, characterization, and theory. Methods for extending the spin and valley lifetime in vdW materials will allow new opportunities in spintronic and valleytronic applications. To explore quantum phenomena, the decoherence mechanisms of quasiparticles (excitons and trions) and the valley index need to be better understood. [268] By patterning either the vdW materials or substrates, new functionalities enabled by metamaterial concepts may emerge. Heterostructures created by vertical stacking or lateral stitching of different vdW materials clearly represent a promising future direction. New opportunities created by exploring interlayer coupling in heterostructures are discussed in detail in the next section. Free carriers, excitons, and valley dynamics are drastically modified in vertical heterostructures. Many TMD vertical heterostructures exhibit type-II band alignment, leading to rapid charge transfer between layers and the formation of indirect excitons. The exciton and valley lifetimes are significantly extended in the heterostructures,[269] providing new opportunities in valley control. Furthermore, quantum emitters due to localized excitons have been discovered in vdW materials.[270-272] The excited states and complex bound states (e.g., biexcitons) associated with such localized states needs to be

understood to explore vdW materials for quantum information applications. Exciting opportunities exist to produce site controlled quantum emitter arrays based on vdW heterostructures. [273]

4.3. Characterizing Interlayer Interactions

In 2D materials, the layers can be separated into building blocks and reassembled either horizontally or vertically to form heterostructures. These heterostructures can either feature the combined functionality of the individual layers or even lead to emergent properties[274, 275] with a range of potential applications, including semiconductor heterojunctions for photodetection and solar energy harvesting.[276-279]

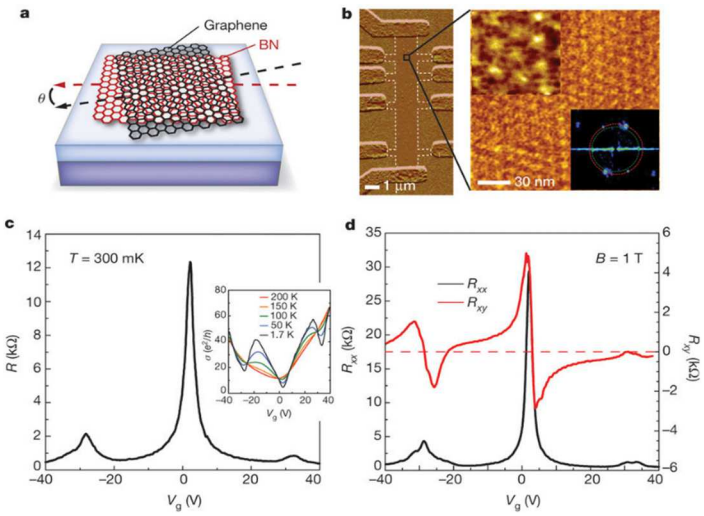

Figure 4.4. Moiré superlattices arise in bilayer graphene coupled to hexagonal boron nitride provide a periodic modulation with length scales of the order of ten nanometers, enabling unprecedented access to the fractal spectrum [14].

The properties of 2D materials can be understood as the combination of properties of individual layers, their structural symmetry, and their interlayer coupling. The latter is very sensitive to the number of layers in the stack and the details of the stacking, such as relative atomic registry and twist angle. In their most stable configurations, homo- and hetero-structures (i.e., stacks between identical and different materials, respectively) adopt a high-symmetry arrangement, such as the Bernal (AB) stacking in bilayer graphene, or AA', 2H, etc. in the TMDs.[280] However, due to the weak van der Waals nature of the interlayer bonding, many metastable configurations with lower symmetry are possible and usually lead to large unit-cell structures, known as Moiré patterns. These configurations can appear during growth or, more generally, can be obtained by stamping techniques with relatively good control. The local interlayer coupling strength changes as a function of interlayer atomic registry. One central research focus in the field of 2D heterostructures is therefore the accurate description of interlayer coupling and its effect on observable properties.

In general, interlayer interactions impact the electronic, excitonic, photonic and phononic (i.e., vibrational) states in vertically stacked vdW materials. Consequently, functionalities can in principle be tuned and optimized by changing the material's thickness and the stacking configurations. Like graphite and graphene, the properties of few-layer 2D materials depend critically on the number of layers.[281] As one example of layer dependent properties, black phosphorus (BP) has an intrinsic thickness-dependent direct bandgap (ranging from 0.3 eV for bulk to 2.0 eV for a monolayer), a property that promises a broad range of optoelectronic applications.[282-285] Manipulating stacking order also leads to fractal quantum Hall effects and van Hove singularities near the Fermi energy, among other effects (Figure 4.4).[14, 232, 286, 287] Notably, the recently observed spin/valley polarization in symmetry-breaking 3R-stacked MoS_2 exemplifies the key role of the stacking sequence in the properties of 2D materials.[288] In another example,

twisted bilayer MoS_2 has been shown to display an electronic structure and exciton/trion behaviors that can be tuned by changing the interlayer twist angle.[289-291] Another recent example is the usage of scanning tunneling microscopy and spectroscopy to probe the interlayer interactions in MoS_2/WSe_2 hetero-bilayers, revealing that the interlayer coupling is indeed a strong function of the interlayer atomic alignment, which results in the spatial variation of the "local" band gap [13]. This result provides a compelling case that Moiré patterns can be used as a new design parameter that has no counterpart in conventional semiconductor heterostructures.

Characterization of 2D crystals has been based on electron microscopy, atomic force microscopy (AFM), and optical spectroscopy methods. Experimental investigations involve probing these properties on multiple length scales -- from atomic to mesoscopic to macroscopic. Fruitful scientific outcomes have resulted from collaborative approaches involving density functional theory (DFT) calculations and multi-scale experimental probes of the controlled formation of vertical stacks (either hetero-bilayers or homo-bilayers). Many studies have utilized optical probes, including micro-photoluminescence (μ-PL), micro-Raman (μ-Raman), and second harmonic generations (SHG) to probe the homo-, hetero- bilayer or multi-layer structures. Such studies have yielded very enlightening results, in particular when the stacking is controlled by variation in twist angles. Among the possible techniques, Raman spectroscopy has the advantage of being fast, non-destructive, and relatively inexpensive, while providing sufficient resolution to yield structural and electronic information at both laboratory and mass-production scales.[292-294] As applied to 2D materials, the majority of early research activities focused on analyzing high-frequency (HF) modes, which involve vibrations stemming from the intralayer chemical bonds.[292, 294-297] However, HF intralayer modes are not very sensitive to the interlayer coupling. In contrast, low-frequency (LF) *interlayer modes* correspond to layer-layer vibrations where each layer moves rigidly as a whole unit with respect to each other. In this case, the corresponding vibrational frequencies are almost solely determined by the interlayer restoring forces. Because interlayer interactions are weak, the corresponding frequencies are usually well below 100 cm^{-1} [274, 298, 299]. These LF modes are categorized into two types: in-plane *shear* (S) and out-of-plane *layer breathing* (LB) vibrations. Due to their greater sensitivity to interlayer coupling, LF Raman modes have attracted attention as sensitive probes of interfacial coupling, including coupling to a substrate. Since the pioneering work of Tan *et al.* in 2012 on multilayer graphene samples,[300] a rapidly growing number of studies have demonstrated LF Raman modes as more effective indicators of the layer thickness,[301-315] stacking order,[298, 316-324] and interlayer coupling in a broad variety of 2D materials. For instance, Chen *et al.* [325] performed helicity-resolved Raman measurements to demonstrate the different symmetry of the LF shear and breathing modes in MoS_2, WS_2, $MoSe_2$, and WSe_2 by controlling the helicity of the incoming and outgoing photons, based on the fundamental property that the LB mode preserves photon helicity, while the S modes reverse it.

There remain significant challenges to achieve high spatial and time-domain resolution, notably using optical probes in characterizing 2D materials. Several near field techniques have been developed. A spatial resolution of ~60 nm in photoluminescence imaging has been reported using the 'Campanile' nano-optical probe. [326] Even finer spatial resolution (~ 30 nm) has been reported using tip-enhanced Raman spectroscopy (TERS) and tip-enhanced PL (TEPL)[327]. These are very promising technical advances. However, the spatial variations in designer heterostructures with Moiré pattern may occur at an even finer length scales below 10 nm. In this context, another promising tool is the use of electron microscopy for high resolution electron energy loss

spectroscopy (EELS). It has been shown that the exciton transition energy can be measured in the EELS spectrum. A spatial resolution of 10 nm has been reported in exciton mapping in 2D materials. [328]

K-space probes of twisted hetero-bilayers have also seen significant progress. By using nano-ARPES to probe $MoSe_2/WSe_2$ vertical stacks with different twist angles θ, Wilson *et al.* [329] reported different band dispersion for the cases for θ = 0° and θ = 30°. This work exemplifies the twist-angle control of electronic structures in hetero-bilayers. However, there is still a big knowledge gap between the real-space and k-space investigations of the electronic structures of Moiré superlattices. Filling this gap will require correlated investigations on the same material system. The knowledge gained would provide a foundation for designer heterostructures using Moiré patterns.

We note that many experimental studies have benefited from a close integration with DFT-based modeling to enable a direct link to the atomistic origin of the observed properties. As the experimental resolution is constantly improving, the enhanced accuracy may challenge existing theories due to approximations made in DFT calculations. For example, existing descriptions of exchange correlation are based on local and semi-local treatment of electron-electron interactions, and DFT is ill-equipped to accurately treat non-local effects governing van der Waals interactions in 2D materials. In addition, first-principle methods cannot routinely treat very large unit cell sizes (of more than a couple thousands atoms) resulting from non-symmetrically stacked/twisted vdW heterostructures. Both these issues are currently subjects of intense research, from a fundamental theoretical and computational point of view. They need to be resolved in order for modeling to offer a predictive guidance to designing vertical vdW heterostructures with specified properties.[295, 330-336]

4.4. New Phases of 2D Matter

The study of novel phases arising from many-body interactions and cooperative couplings between different fundamental degrees of freedom is of great significance for electronic materials and has produced recent breakthroughs in vdW materials. For example, the discovery of enhanced superconductivity induced by substrates or external fields, including high-T_C superconductivity below 65 K in monolayer FeSe on $SrTiO_3$, has spawned a large body of research. [337, 338] Moreover, electrical gating has been used to induce enhanced superconductivity in TMD band insulators such as MoS_2 at densities inaccessible by chemical doping. [339] Such ion-gated TMDs provide evidence for Ising superconductivity with a vastly increased critical magnetic fields. [340, 341] In monolayer TMDs, the oppositely-aligned spins of the electrons forming a Cooper pair are protected by the correspondingly reversed spin-orbit splitting at the K and K' valleys. Novel cooperative phases have also been discovered far away from equilibrium, as exemplified in recent studies of light-driven charge density waves (CDW) in TaS_2.[5] In equilibrium, charge density modulations accompanied by star-shaped polaronic lattice distortions result in a nearly commensurate CDW phase, which transitions into commensurate ordering below 180 K. Intriguingly, this low-temperature CDW phase was found to transition into a 'hidden' metallic state upon optical excitation (Fig. 4.5), resulting in a novel meta-stable, ordered phase which is inaccessible in equilibrium. [5, 342]

Significant opportunities exist in both discovery of cooperative phases in vdW materials and in seeking novel applications. Switching between correlated phases with optical or current pulses provides one example, motivating further fundamental studies of photo-induced phase transitions

and novel concepts for low-energy electronics. Complex vdW heterostructures represent a unique opportunity in that new physical properties can be expected from atomic-scale couplings that extend beyond those of the individual dielectric, metallic, superconducting, magnetic, or charge-ordered layers. The few-layer nature of vdW superconductors provides an ideal testbed for the theory of phase transitions in 2D and may allow construction of novel lateral and vertical heterostructures with directed confinement and control of quantum coherent phases. In TMD superconductors, Ising spin-orbit coupling has been predicted to result in exotic types of spin-triplet Cooper pairs which may enable topologically nontrivial superconducting phases. [343] Moreover, long-range quantum coherence can arise from polaritons or exciton condensates, for which TMD heterostructures may offer a unique platform as mentioned below.

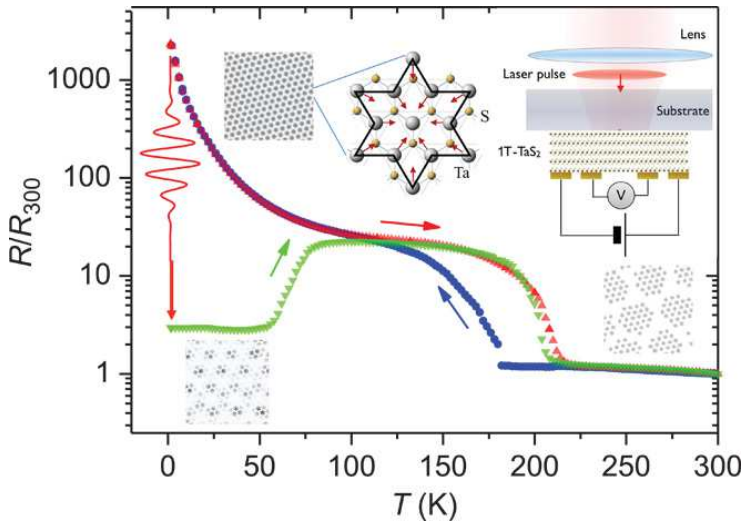

Figure 4.5 A single light pulse drives the low-temperature charge-density-wave state in TaS_2 into a meta-stable 'hidden' phase, accessible only via non-thermal pathways. The ordering of star-shaped polarons is indicated, including the tentative ordering for the hidden state. [4-6]

There are many challenges to address to advance the exploration of new phases in 2D materials, including the growth and assembly of high quality vdW layers and heterostructures, understanding the role of defects, disentangling and modeling the complex physics of cooperative quantum phases, and developing and applying relevant advanced characterization techniques. For example, the intriguing superconductivity in FeSe/STO sensitively depends on the interfacial doping and vibrational properties, which necessitate careful fabrication steps and a UHV environment. [338, 344] Advanced surface-sensitive techniques such as ARPES and STM play an important role, but access to buried interfaces is equally important to probe complex heterostructures. Other important challenges include clarifying whether cooperative phases persist in vdW layers within heterostructures or when manipulated by external perturbations. Unraveling such complex physics requires research combining advanced theory, growth, and characterization with high spatial, time, or energy resolution.

The study of novel 2D phases will benefit both from the exploration of the phase diagram of monolayer and few-layer vdW materials subject to external stimuli such as electric, magnetic and optical fields, as well as from the design, fabrication and characterization of vdW multilayers with new properties. An example of the latter includes TMD heterostructures that host spatially separated, interlayer excitons with long lifetimes (Fig. 4.6), which was proposed as a platform for novel excitonic circuits and exciton Bose condensates at record high temperatures.[345] Interlayer excitons with nanosecond lifetimes have recently been demonstrated in TMD heterostructures utilizing bias control or type-II band alignment for electron-hole separation across the interface.[346, 347] Excitonic circuits were previously studied in quantum wells, and further progress may extend such physics to TMD systems and ultimately enable electron-hole superfluids and exciton condensates up to ≈100 K. Intrinsic ferromagnetism has also been observed in 2D vdW crystals, [348] which is of interest for spintronic applications. Tuning through van-Hove singularities within mini-bands may lead to enhancements in collective phases such as superconductivity or magnetism. Overall, the field should continue to encompass a broad range of experimental and theoretical work, spanning the range from discovery to control of novel cooperative phases along equilibrium and non-thermal pathways.

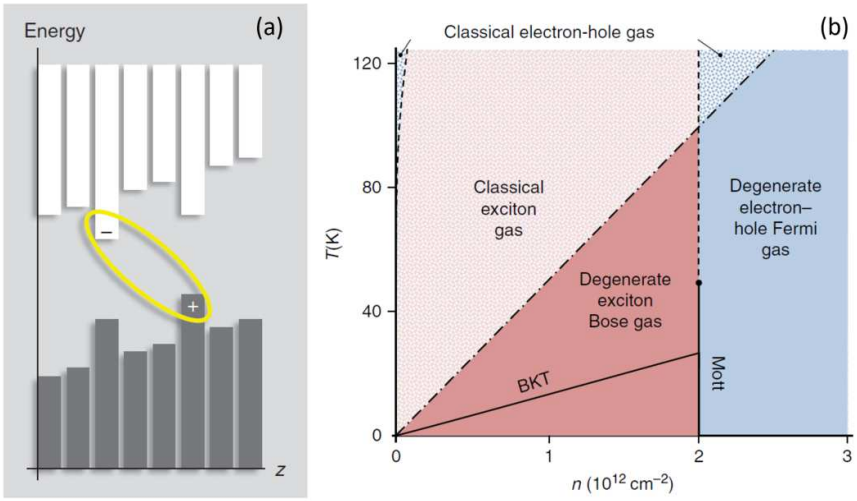

Figure 4.6. (a) Spatially-indirect excitons in vdW heterostructures, theoretically predicted to allow exciton Bose gases to exist at record high transition temperatures (which scale directly with the enhanced exciton Rydberg energy in vdW materials). (b) Schematic phase diagram. [345]

4.5 Cross-Cutting Opportunities and Impacts

In addition to the topics described above, the workshop participants also identified several new directions that deserve more attention due to their potential to advance the goals of complementary research areas in the EPM portfolio and their transformative potential. In general, vdW materials present many opportunities to go *beyond single-phase materials*. This promise is already being vigorously explored in vdW vertical heterostructures, as discussed above, but there are further opportunities in mixed-dimensional vdW heterostructures. The concept of "Coulomb engineering" of vdW properties via the dielectric environment can be expanded to consider patterning of metals and dielectrics to create new metamaterials with engineered effective permittivity and permeability. There is also an opportunity to create new functional organic/inorganic interfaces with degrees of freedom beyond crystal orientation where epitaxy is not necessary to define useful junctions.

Several cross-cutting challenges were identified that would enable progress in the areas described above. The ability to grow monolayers epitaxially over large areas, and grow in selective areas,

would be enabling for all research themes described above. For both growth and transfer processes, understanding of defect formation and mitigation is very incomplete. The challenges here are to understand the novel physical phenomena associated with defects and interfaces, develop synthesis and nanofabrication approaches to control their formation and employ atomic-level characterization methods to study their local structure and chemistry. Moreover, there is a need to determine the limits of single particle descriptions and when many-body effects must be considered: challenges include not simply determining what computational effort is necessary, but also how to interpret experiments. Finally, it remains challenging to identify the most compelling applications to pursue. In the case of advanced memory and logic devices that go beyond complementary metal oxide semiconductor (CMOS) technology, there is no clear roadmap to follow. Further industry input on applications in, for example, flexible electronics could stimulate impactful research and provide useful benchmarks for comparison with more established materials in that space, such as organic semiconductors.

One of the most significant *emerging* technology areas, and one of vital interest to national security, encompasses quantum technologies (QT), including quantum communication and quantum computing. This has been recognized in the E.U. by the Quantum Technology Flagship initiative, in which vdW materials may be utilized to build essential components needed for QT. For example, the "Nanoscale Systems for Optical Quantum Technologies" project in Horizon 2020 aims to build nanoscale hybrid quantum devices that strongly couple to light, and graphene-based hybrid devices show particular promise. In the U.S., NSF has identified "The Quantum Leap: Leading the Next Quantum Revolution" as one of 10 Big Ideas for Future NSF Investments, but currently no national initiative exists in this vitally important area. However, NSF has recently made significant investments in infrastructure that can support vdW materials research. In particular, the establishment of the Materials Innovation Platforms, Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARDIGM) at Cornell and 2-Dimensional Crystal Consortium (2DCC) at Penn State, directly address many of the fundamental cross-cutting challenges in growth and characterization as described above.

The Materials Genome Initiative (MGI) aims to create a new era of policy, resources, and infrastructure that support U.S. institutions in the effort to discover, manufacture, and deploy advanced materials twice as fast and at a fraction of the cost. The MGI has guided federal agency investments that impact vdW research through funding opportunities, research facilities, collaboration resources, and materials databases. For example, the Center for Hierarchical Materials Design (CHiMaD) includes a user group on "Low-Dimensional Nanoelectronic Materials" that seeks to understand and realize p-type and n-type doping in vdW materials. Database development efforts in CHiMaD and NIST can help capture the value of research funded by the federal government as well as industry consortia such as SRC. For example, NSF funds vdW materials research through the EFRI 2-DARE and DMREF programs, and the findings could be shared with the vdW research community in standardized formats by leveraging new databases. Additionally, users of the MIP are *required* to share data generated with MIP infrastructure following publication. Hence, the MGI framework provides mechanisms for NSF funded research to provide greater benefits to society by making data more useful and accessible.

The National Strategic Computing Initiative includes an objective to "Establish a viable path forward in the 'post-Moore's Law' era." NSF has made investments relevant to this strategic

objective, such as the Energy-Efficient Computing: from Devices to Architectures (E2CDA) program, and vdW materials are being explored in some of these projects. There have been reports of devices based on vdW materials being utilized to implement synaptic or other neural functions. Research of vdW devices for neural functions has thus far focused primarily on imitation of behaviors, and thus one important future direction involves large-scale functional demonstrations. While the Brain Initiative does not directly support vdW materials research, the goals of understanding brain function and how it differs from existing computing paradigms can help guide exploration of alternative computing schemes using vdW materials. Furthermore, electronic materials in general are important in probing brain function in a number of modalities, and electronic devices and circuits are being developed that more closely emulate brain-like computing, providing an opportunity for understanding the brain by developing systems of increasing complexity.

5.Organic and flexible electronics materials

5.1. Introduction

Organic and flexible electronics materials are enabling versatile platforms with great promise for cost-effective and potentially environmentally friendly manufacturing of future technologies. These include electronic and photonic components, such as printed radio-frequency identification (RFID) tags and memories; wearable or "imperceptible" electronics; ultrahigh mobility transistors that allow new, low-cost, large-area computation technology; large-area lighting applications but also electronically pumped lasers; building-integrated photovoltaics and off-grid solar panels; smart packaging products, *e.g.*, for sensitive products such as food and drugs; smart labels for counterfeiting protection or logistics purposes; compact and skin-compatible analytical systems that enable continuous monitoring for, for instance, medical diagnostics or environmental analysis; to name but a few examples [349-364]. The possible applications for such components are indeed wide-ranging and fascinating; for instance, their use in an autonomous intelligent environment by the 'Internet of Things'—human/machine interfaces, electronic skins, wearable electronics and beyond—can be readily envisioned.

This ambition has been fueled by the development of a plethora of new materials and materials platforms that have allowed the broad field of organic and flexible electronics to produce great scientific and technological progresses—here in the U.S. and world-wide—leading to a number commercial successes as witnessed, for instance, by the rise of organic light-emitting diodes (OLED) for smart-phone and television displays. Many organics-based technologies also out-perform metal oxides (*e.g.*, InGaZnO) at plastic-compatible temperatures[354, 355, 365-368], making them more appropriate for use in high throughput roll-to-roll fabrication on flexible substrates. Fundamentally, organic and flexible materials platforms are also of great interest. Complex photophysical processes occur in these multifaceted materials systems (charge generation/recombination; light emission; polaron coherence; possibly, hybrid excitons and polaritons)[350, 359, 369-371]; and they may sustain multiple charge transport mechanisms (electronic-, ionic-, mixed conduction)[19, 372-374]. They feature intricate processing/structure/property interrelations (*e.g.*, the dependence of overall properties and device performance on multi-scale structure)[19, 20, 370, 375-378]. Many, versatile interface phenomena can also be exploited (*incl.*, injection phenomena and work-function tuning)[379-383], and intriguing signal transduction possibilities are offered (*e.g.,* ionic-to-electronic [384-387]). Finally, processing and other environmental conditions can be used to fine tune and optimize the overall properties and device function (*e.g.*, through use of nucleating agents, annealing procedures or exposure to aqueous

environments with high ionic strengths). In short, it is clear that the organic and flexible materials platform offers exciting and fascinating opportunities.

Yet, because of this versatility, breadth, and growth potential, realizing step changes—fundamentally and/or technologically—can be challenging and often requires approaches across the entire materials chain: from materials design and synthesis, materials characterization, with the correlation of processing, structure and properties, materials theory and modeling, device fabrication and characterization, to prototype manufacturing and product development. Indeed, in many cases only cross-cutting approaches can provide the required synergies. Various materials options towards organic and flexible electronic systems need thereby to be considered. Weakly interacting polymeric and small molecule organic semiconductors were possibly the first viable entries and continue to be of great interest[388-392]. Increasingly, 2D- and 3D- metal halide perovskite materials (where interactions between moieties can be strong) and, for instance, semiconductor nanocrystalline materials (which can be weakly interacting depending on the passivating ligands)[352, 356] are attracting attention as well, because they are demonstrating certain properties that may also lead to their incorporation into new, flexible electronic and photonic technologies. Unique prospects exist to exploit these different materials platforms in existing technologies as well as for applications inaccessible to conventional semi-conductors. The reason is that organic and flexible materials platforms can easily be modified in a seemingly infinite variety of ways to tune not only their optoelectronic properties but their entire property sets (including, for instance, their mechanical and biocompatible characteristics; see Figure. 5.1). This tuning can be achieved, e.g., via changes in the molecular and macro-molecular chemistry, their assembly and molecular packing, the design of organic/inorganic hybrid materials, and/or the engineering of relevant interfaces. However, this multitude of options also renders the establishment of a deep understanding of these materials systems an intricate task. Therefore, it is not surprising that rather pronounced knowledge gaps still stifle progress in the area of organic and flexible electronics, and a lot of the necessary physical understanding of organic and flexible materials, as well as of the devices and components made of them, is too often still lacking.

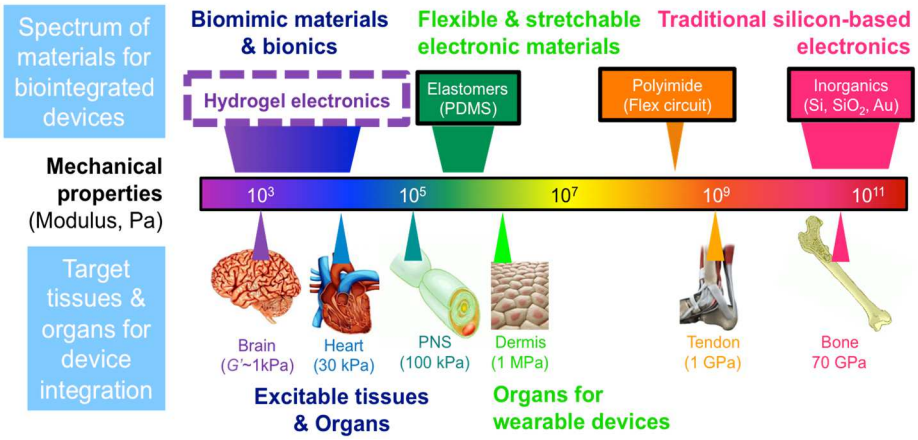

Figure 5.1 The properties of organic and flexible electronic materials can readily fine-tuned via fine-tuning of chemical structure and molecular assembly. This allows, for instance, harmonizing mechanical properties for applications in the biointegrated electronics/bioelectronics area. Materials traditionally used in microelectronic device fabrication (e.g. silicon, oxides, and metals) exhibit Young's moduli that are orders of magnitude larger than the tissues with which they are intended to interface. There are, thus, opportunities to engineer elastomeric and hydrogel-based electronic materials for applications in wearable and implantable devices, respectively.

Knowledge gaps in this area arise from several different directions; three of the main ones are summarized below:

- The lack of understanding and control of intramolecular and intermolecular order and interactions within specific materials, which critically dictate properties and features important for device performance and component functioning. Examples include charge transport (*cf.* Figure. 5.2 as an example), charge generation and/or light-emission, as well as the general optoelectronic landscape (*e.g.*, densities of mid-gap states which control charge trapping and recombination).
- The lack of understanding and control of interfaces, including the energetics at interfaces or the dynamics of charge transfer at molecular and supramolecular interfaces (for instance, between active layers and charge collection/injection contacts), which all are critical for the creation of efficient and robust logic-, display- and energy conversion- platforms.
- The lack of capability to reproducibly deposit organic and flexible electronic materials and pattern them with required resolution.

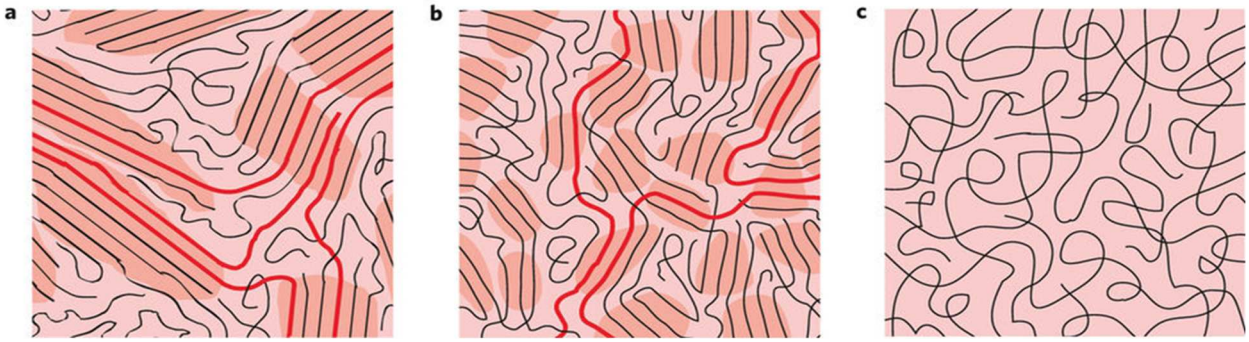

Figure 5.2. Schematics of some of the microstructures that a polymer semiconductor can adopt. From a semicrystalline microstructure comprising relatively well defined crystalline moieties (a), to structures that comprise more disordered aggregates beside the amorphous fraction (b), and a completely amorphous assembly (c). Note the coexistence of ordered (darker shadowed areas) and spaghetti-like amorphous regions in scenarios a and b. This microstructure is similar to the concept of fringed micelles. If the molecular weight is high enough and there is a large enough density of ordered material, long polymer chains (highlighted in red) can connect ordered regions without a significant loss of conjugation, greatly improving charge transport. Figure adapted from Ref [19]

There is still some way to go before the full potential of organic and flexible electronic materials systems can be widely exploited—not only fundamentally, but also technologically. The reason is that this lack of fundamental and applied knowledge leads to issues not only concerned with, *e.g.*, materials discovery and device design, but also with future manufacturing and scale-up (including product yields, satisfactory lifetime and stability). Indeed, while display applications using organic light emitting diodes represent a spectacular success, similar approaches for future technology platforms are still challenging. It requires emphasis on fundamental aspects of materials science, chemistry, physics and device engineering. On the technology side, the requirements for versatility, efficiency (*e.g.*, electricity-to-light conversion), stability (*e.g.*, color stability of displays) and speed (*e.g.*, for flexible logic) for future innovations need to be met based on improved fundamental knowledge.

Here, the promise and potential impact of organic and flexible materials are discussed in the context of the NSF DMR EPM program and beyond. Recent breakthroughs are summarized, and challenges and bottlenecks debated. Approaches to address these challenges are proposed, and future opportunities and promising directions suggested, with the objective to contribute to a

discourse on the current challenges and future opportunities in electronic and photonic materials, with focus on organic and flexible materials platforms.

5.2 Promise and potential impact

Flexible and/or organic electronic and photonic technology platforms could have wide-ranging impact on our daily life—especially when traditional limitations of their inorganic counterparts, generally imposed by size, weight, and compatibility, can be overcome. *Organic materials* and devices are already shaping the field of electronics. Nowhere is this more apparent than in the mobile electronics market where OLEDs are fast becoming the dominant display technology. They are also making rapid inroads into televisions, monitors and even solid-state lighting. Following developments in OLEDs, organic photovoltaics (OPVs), now reaching efficiencies of close to 15%[349], are poised to enter the emerging and potentially vast building-integrated and building-applied solar markets. Less clear to date is the application space for organic thin-film transistors (OFETs). While they have shown performance exceeding that of amorphous Si by a wide margin, a unique application has yet to be found. Sensor circuits, *e.g.*, for medical applications appear to be promising, as they take advantage of the materials' flexibility, possible biocompatibility and biodegradability, and their potential to be manufactured over large areas at low cost. Moreover, many new trends that lead away from the traditional applications of organic and flexible materials systems emerge, which take advantage of the interplay of electronic, ionic and energy transport in organic and flexible materials. New fields of interest for flexible materials systems are thus evolving, directed among other things towards use in bioelectrics[393], electrochromics[387] or thermoelectrics[394]. These applications rely in many cases on the interactions between ions and electrons in the material (Figure. 5.3). Indeed, it is often required that ions be able to penetrate the bulk of the active (organic/flexible) materials for such interactions to occur. The basic working mechanism is akin to electrochemical doping. If an anion penetrates, for instance, a polymer semiconductor—one of the most used organic materials platforms—because of an electrostatic field, it must be compensated by a positive charge: a mobile hole in the conjugated polymer. As a result, the material becomes more conducing as it becomes *p*-type doped.

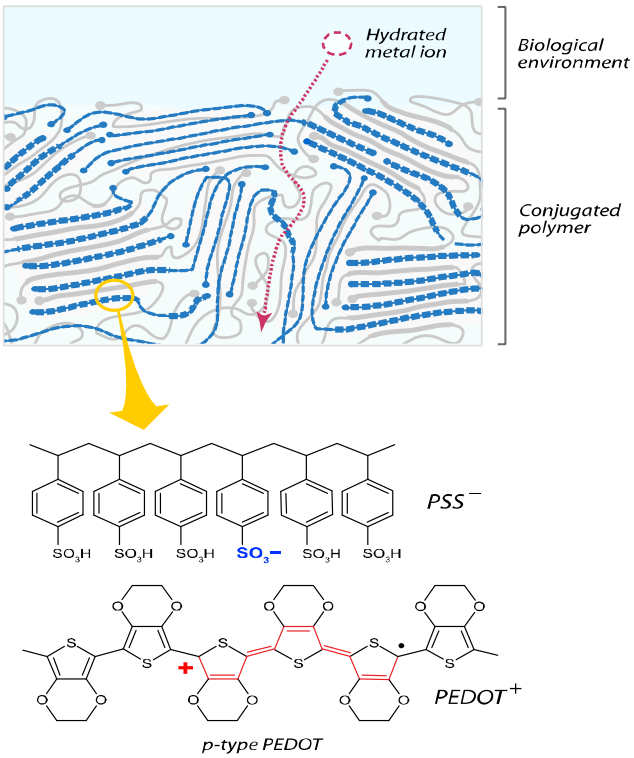

Figure 5.3 Schematic of the interaction of ions and a mixed conduction polymer (PEDOT:PSS) in an aqueous electrolyte, showing the potential, different charge transport pathways. Figure adapted from Ref. [8]

Many devices can be envisioned that rely on this basic principle. *Transducing ion fluxes into electrical currents* allows, for instance, to realize highly responsive neural probes[384]. Similarly,

modulating the conductivity of organic material systems with ions is the basis for highly sensitive ion sensors[386]. Because the neutral and oxidized states of these materials typically have different colors, the introduction of ions, which alters the charge state of the polymer, also induces color changes, leading to fast-responding electrochromic devices[387]. Furthermore, the relatively high doping density that can be induced with ions may be advantageous for thermoelectric applications, which require high electrical conductivity and low thermal conductivity[394]. Finally, the combined ionic and electronic functionality is attractive for making polymer electrodes for batteries[385, 395].

One basic device that takes possibly most advantage of mixed ionic and electronic conduction and has great promise, is the organic electrochemical transistor (OECT)[396]. This device has the basic functionality of a transistor (*i.e.*, the voltage on a gate electrode modulates the conductivity of a polymer channel), but displays some important differences compared with conventional field-effect transistors. The gate electrode is immersed in an electrolyte, which, when polarized, induces ionic motion. If the electrolyte swells the polymer, ions penetrate the whole volume of the polymer, giving rise to an extremely high total capacitance as the polymer acts as an ion sponge[397]. The resulting amplification of the transistor, characterized by its transconductance (= dI/dV_g) is therefore much larger than in conventional field-effect devices[372]. The trade-off is given by the fact that ionic motion is slow, therefore OECTs operate at frequencies on the order of tens of kHz at most. Applications of OECTs must take into consideration this fundamental limitation. Importantly, the device operation can be reversed, and one can use an electrical current to drive an ion flux, essentially making electronically controlled ion pumps [398]. These devices have been proposed to deliver therapeutics on demand, at the push of a button or as a result of a sensing event in a closed-loop system. Finally, the analogy between the working principle of OECTs and the communication between neurons across synapses has inspired the use of mixed conductors in artificial synapses for neuromorphic computing with exceptionally low switching energies[364, 399].

One can furthermore envisage *bio-integrated devices* intended to interface directly with the tissue and organs of living systems. Hence, such devices are often required to be mechanically soft and flexible. Their interest stems from possibly enabling a wide range of diagnostic and therapeutic functions including distributed biosensing, physiological monitoring, and brain-machine interfaces. Moreover, flexible and biointegrated electronics have the potential to advance 3 of the 14 grand challenges set forth by the National Academy of Engineering (NAE): (*i*) To reverse-engineer the brain; (*ii*) to engineer better medicines; and (*iii*) to advance health informatics. Flexible and biointegrated electronics, in the form of wearable and implantable medical devices, could also be targeted to monitor neural functions in the central and peripheral nervous systems (which was alluded to above), thus, serving as integral technology platforms to advance "bioelectronics medicines"[400, 401]. Moreover, they can collect vast amounts of data, allowing patients and healthcare providers to make better informed decisions.

The few examples given above illustrate the impact that organic and flexible electronics can have in a wide variety of areas, from energy harvesting and storage, to sustainable living and green cities, and health care. In addition, new possibilities continuously arise. For instance, alternative materials systems are advanced and/or re-discovered, from *solution-processable quantum dots or metal halide perovskite systems to other 2D materials.*[352, 356, 402-405]Many of these are poised to assume a critical role in the development of future flexible technologies, such as new quantum information systems based on formation and detection of "entangled photons". Intrinsic problems to overcome here are: *i*) Realizing the generation of entangled photons (arising from systems which demonstrate high levels of optical nonlinearity, *e.g.*, graphene and other 2D constructs such as

single or few-layer GaSe, MoS_2, BN, *etc.*[406, 407]); and *ii*) achieving the detection of a few entangled photons in a larger ensemble of uncorrelated photons. Integration into conventional silicon photonics platforms should also be considered[408].

In summary, various science and technology quantum leaps can be expected in the organic and flexible electronics field. There are, however, many fundamental and technical challenges that must be addressed first in order to fully exploit the potential of this broad and versatile materials and device platform.

5.3 Recent breakthroughs

The past few years have brought important advances in the field of organic and flexible electronic materials on both experimental and theoretical fronts. Fundamentally, our understanding of relevant electronic and optical processes at the molecular scale and nanoscale and their connection to key structural features (molecular arrangements, supramolecular packing, phase morphology and microstructure) has drastically improved. For instance, insights into the energy loss mechanisms[369] limiting organic solar cells have been gained and quantitative interaction/miscibility-function relations for donor:acceptor systems have been established. These advance have allowed the field to establish better materials selection criteria for OPV device fabrication[409, 410]. Another illustrative example is electronic charge transport in semiconducting polymers—one of the key materials class amongst the large library of organic and flexible electronics systems. A notably better knowledge has evolved of the structural features that determine charge transport in this class of materials[19, 20, 377] (Figure. 5.4); based on both experimental and theoretical work, a coherent picture has emerged about the role of energetic (static and dynamic) disorder. As a consequence, charge-carrier mobilities in thin films of organic and flexible electronic materials have risen steadily in the last decade, owing as well to better control of charge injection/collection contacts, to the point where hole- and electron-mobilities in certain platforms can exceed 10 $cm^2/V{\cdot}s$—more than adequate for a variety of low-level digital FET-based logic circuits[356-358, 389, 411], as will also be discussed below.

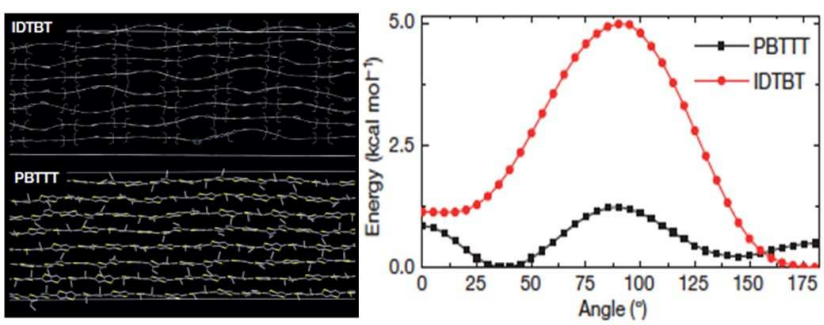

Figure. 5.4. Comparison of two semi-conducting polymers that illustrates the importance of the resilience of torsion-free polymer backbone conformation to side-chain disorder. The IDTBT polymer has a higher barrier to torsion and a smaller difference in Urbach energy between disordered and amorphous states compared to PBTTT leading to more ideal transport properties. The side chains and hydrogen atoms are omitted for clarity. Figure adapted from Ref[20]

A strong contribution towards this understanding originated from great progress in how we process and deposit organic and functional materials. In many cases, we have gained the tools for controlled deposition of organic and flexible electronic materials into desired structures. The deposition can be achieved through exploitation of classical materials tools that permit fine-tuning of both structural features on the nano- to the micronscale (via selection of printing and solution deposition conditions[411-413], assist with the control of the materials solidification employing additives and/or use of phase diagrams, blending, *etc.*[409, 410, 414-416]) as well as enable the realization of complex architectures (*e.g.,* via 3D-printing, micromolding, embossing)[412, 417-419].

Critical for this progress has also been the advancement in the theoretical and computational methodologies applied to organic conjugated materials[420]. In the field of density functional theory, for example, the development of robust range-corrected functionals including dispersion terms, has allowed a reliable description of the geometric structure of extended π-conjugated systems and of the nature of their intermolecular interactions. This development has led to advances in understanding the physics of charge generation in organic photovoltaics or of light emission in organic light-emitting diodes based on fluorescence, phosphorescence and thermally assisted delayed fluorescence (TADF). A comprehensive understanding of energy and charge transport in both crystalline and amorphous π-conjugated systems has been reached via methodologies addressing the coupling between electron excitations and both intra- and inter-molecular vibrations as well as the influence of static and dynamic disorder. Moreover, methodologies combining molecular-scale electronic-structure calculations with nano-/meso-scale molecular dynamics simulations inform on the impact of the "local" morphology on the electronic states playing a role in charge generation, recombination, and transport. These advances have opened the way to the description of quantum coherence effects, for instance in the case of charge separation in OPV. This progress has also resulted in the development of more realistic device modeling tools, also in the case of OLEDs and OFETs.

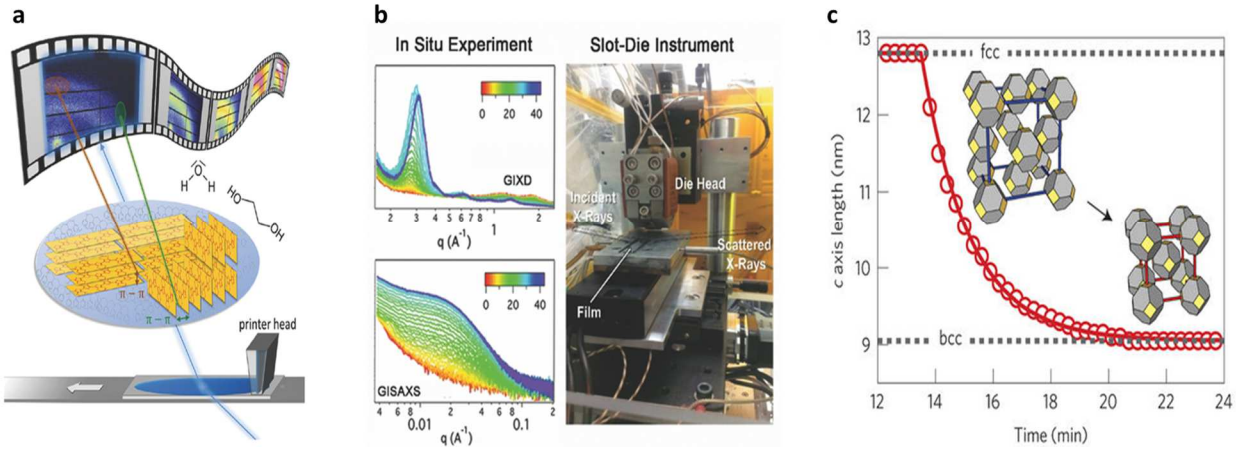

Figure 5.5. (a) Schematic illustration of an in situ GIWAXS setup, recording structural changes during film formation. The thin-film structure is detected, e.g., in terms of the π–π stacking distances in case of organic semiconductors, as depicted in the close-up. (b) In-situ GIXD and GISAXS can also assist with in-situ characterization of blends. Scattering profiles are shown of a donor:acceptor bulk heterojunction blend wet-film during the drying process. The wet film is slot-die coated at the synchrotron station. The substrate is pre-aligned and X-ray is continuously applied during the film coating and drying process. (c) Information can also be obtained on other classes of flexible organic materials, such as lead sulfide (PbS) nanocrystals. Shown here are the kinetics of structural rearrangement during their self-assembly, deduced from GIWAXS patterns. Figures adapted from Ref 422, 410, and 376.

Another important factor in the improvement of our understanding of organic and flexible electronic materials is the advances in characterization tools (see Figure. 5.5 for some examples) and metrology that allow *in situ* analyses of thin films and more complex structures, *e.g.*, during film formation or device operation. For example, improved spectroscopic measurements have enabled the elucidation of the relevant energetics in materials of interest, assisting in unraveling the critical role of interfaces in organic/flexible material architectures. Structural studies have uncovered the role of molecular packing, domain interfaces (including molecular orientation at

such interfaces), grain sizes and orientations, and the overall size/tortuosity and purity of phases (*e.g.*, in heterojunctions). Reflection-mode X-ray scattering methods (GISAXS and GIWAXS, to study nano- and molecular structure, respectively) have been successfully deployed to elucidate thin films of organic and/or flexible electronic materials, allowing quantification of structural order in highly crystalline or semi-ordered materials. Such X-ray techniques can quantify many aspects related to defects and disorder [19, 421]. When combined with X-ray resonance, these techniques can resolve where the various components localize [422]. Recently, in-situ studies of materials *during* the film casting process have in particular helped in shedding light on the critical role of process history in determining the final micro-structure [378, 412, 423, 424]. These studies of materials during formation and transformation are especially valuable given the non-equilibrium configurations required for optimal performance in many cases.

Advances have also been made in materials design and development. For instance, in the OLED area, important first steps towards long-lived blue emitting materials that could enable high-efficiency lighting that lasts tens of thousands of hours, have been made by a combination of physics- and chemistry-based insights. Particularly, the use of "managers" to reduce triplet exciton-polaron annihilation reactions that degrade blue phosphorescent OLED performance, has made a dramatic difference in OLED lifetime. [350, 351] Phenomena, such as TADF, open up new opportunities [371, 425]. In solar energy generation, the introduction of non-fullerene acceptors has led to a burst of improvements in the efficiency of single-junction solar cells, now exceeding 13%, [349] with multi-junction cells expected soon to break the 15% efficiency threshold; in OFETs, very thin dielectrics have led to the demonstration of complementary logic operating at <1 V. [360]

Bioelectronics research has also made great strides, for instance, in the creation of truly flexible or even foldable materials; achieving certain specific processes such as biomimetic signal transduction; and developing processes that allow device integration. Indeed, the form factors and intrinsic mechanical properties of electronic materials have evolved dramatically from the initial generations of integrated devices that are fabricated on bulk silicon with brittle mechanical properties and planar form factors (Figure 5.1). The advent of organic-based active layers has enabled flexible devices, [361, 426] and integration onto water permeable substrates (~1-µm thick) has indicated the applicability of organic, flexible electronic materials to skin-wearable electronics and medical sensing applications. [353] For this purpose, transfer printing techniques have been advanced to integrate silicon-based active layers with elastomeric substrates, enabling new capabilities such as stretchable and highly deformable devices [417, 427]. These techniques have been extended to other mechanically compliant materials including hydrogels, which can further expand the parameter space for <u>*mechanically compliant electronics*</u> (Fig. 5.6) [418]. With respect to bio-mimetic signal transduction, there have been many exciting advances in materials that can modulate the flow of ions and protons, which is the primary information currency for living organisms[428]. Novel conducting polymers and bio-electronics media can sort, measure, and transduce ionic and protonic currents into electronic signals[8, 429-431]. Reliable signal transduction is critical when converting signals from tissues and cells into the synthetic realm of digital computation. As discussed above, the development of OECTs operating with a very high transconductance [372] (higher than any other transistor technology reported) is thus important—as examples for neural sensing [384] have demonstrated. Furthermore, the integration of the capability of sensing and delivery in a single "neural pixel" unambiguously provides a first step towards a closed-loop sensing-therapy system [362]. Ion pumps to deliver small molecules in live animals illustrate that tight integration of electronics and biochemistry is possible; the artificial synapses that have been recently reported, are excellent demonstrations that different levels of functionality, from short-term potentiation to long-term potentiation, multi-state

memory and simple pattern recognition [364, 399, 432], can be achieved. Further examples of successful biointegrated electronics are based on the fact that they can leverage biomaterials as functional components in biomedical devices such as power supplies[433-435] bioactive sensing elements [363, 436] and biodegradable circuits [437, 438].

Finally, it is worthwhile to highlight a few recent breakthroughs in the area of *doping* [439]. Doping is crucial as all technologies discussed above usually rely on the ability to spatially control the charge density in specific locations. This is generally achieved by doping. Doping in organic electronic materials is fundamentally different than in conventional semiconductors as it is generally a chemical charge transfer process—*i.e.*, dopants are not substitutional as in inorganic semiconductors. Doping has been highly enabling and contributed to our understanding of, *e.g.* interfaces. It also has been highly enabling for OLEDs. This is due to the fact that a large variety of *n*-type dopants have been put forward over recent years, while until a few years ago only *p*-type dopants existed. Moreover, new stronger *p*-type dopants have been developed, thereby expanding the palette of dopant materials [440]. This has partly been contributed to the many new processing techniques that have been devised to allow doping organic and flexible electronic materials platforms without substantially altering their microstructure. Indeed, too often, if one mixes dopants and polymers in solution, they aggregate and precipitate as they form a salt which is insoluble in most typical organic solvents used to dissolve the polymer [441, 442].

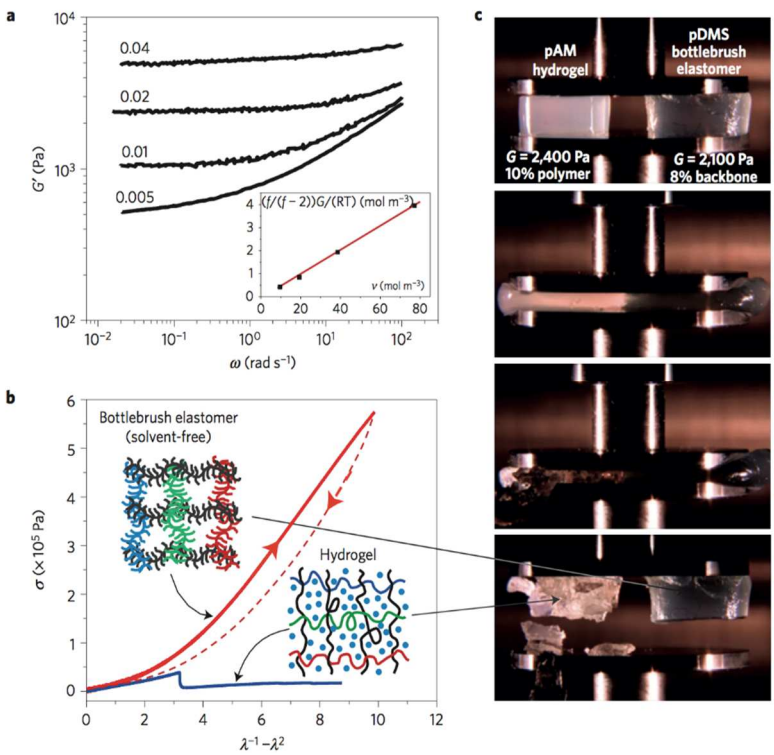

Figure 5.6. Supersoft and superextendable elastomers may be rendered electronic in future. Herem the diversity in mechanical properties are demonstrated. (a) Poly(dimethyl siloxane) (pDMS) bottlebrush elastomer sexhibit moduli of the order of 100–1,000 times softer than linear pDMS. Inset: the plateau modulus decreases with calculated crosslinking density, where the slope gives 5% crosslinker reactivity and the zero-intercept suggests about 10% of dangling strands. (b,c) True stress and compression behavior of such gels made of pDMS bottlebrush elastomer. Figures adapted from Ref [16]

The resulting microstructure is non-uniform and only very thin polymer films can be deposited. If the dopant on the other hand is deposited after the polymer film has been processed, from a solvent that merely swells the polymer without dissolving it, the dopant penetrates the film without altering its microstructure. This process is called sequential doping [443, 444]. An alternative to sequential doping is vapor-phase doping, where the dopant is thermally evaporated onto the semiconductor and diffuses in [445]. These two processes have contributed to the recent step changes that have been

achieved such as realization of very high conductivities due to an unperturbed polymer microstructure and higher dopant concentration. Furthermore, low-resistance contacts have been produced for short-channel transistors and inversion-type devices can be created [446]; also, light doping can be exploited to increase overall device mobilities in, *e.g.*, transistor devices as it can promote trap passivation [447].

5.4 Challenges and bottlenecks

Fundamentally, one key challenge for most devices based on organic and/or flexible materials is the fact that they rely on active layers consisting of electrically and/or optically active π-conjugated molecular or polymeric materials. The π-conjugated molecules or polymer chains are held together by weak van der Waals interactions (mainly dispersion forces, often referred to as π-π interactions). This inherent characteristic has the benefit of promoting flexibility and stretchability but also results in varying degrees of disorder (or, in the case of crystalline materials, the presence of polymorphs). Thus, it comes as no surprise that the main successes to date in machine learning and materials genome areas relate to inorganic, fully covalently bound materials rather than π-conjugated systems and other classes of flexible electronic materials.

Interfaces can lead to further complexities. In the case of molecular semiconductors, electrical contacts with low work functions (to optimize electron collection/injection) and contacts with high work functions (to optimize hole collection/injection) can cause partial or full integral charge transfer that can be hard to predict and control[379, 380]. For structures made of other flexible electronic materials platforms such as *2D- and 3D- metal halide perovskites*, very different valence and conduction band edge energies at heterojunctions with electron- or hole-harvesting contacts are frequently observed. These energies may be explained with these materials' open shell and polar low-index terminations, making them extremely reactive toward contacts such as those routinely used with organic materials. The chemical reactions that thereby can occur at these interfaces range from Lewis and Brønsted acid/base chemistries, adsorption of ions, and redox processes, destabilizing such heterojunctions [381]. These effects combined make it very challenging to establish clear relationships in the bulk and at interfaces, among chemical structure, electronic properties, morphology, processing, and ultimately performance.

Structural analysis, while having seen notable progress with new and further developed methodologies drastically assisting progress in the field of organic and flexible electronics materials, still encounters its own challenges. This is predominantly due to the fact that many organic and flexible materials platforms are of low molecular order. Hence, they do not give rise to a distinct signal in scattering/diffraction techniques, and are difficult to resolve even in direct imaging methods. However, there is an opportunity for the community to take advantage of recent advances in electron microscopy (EM), especially the development of low-dose imaging (via direct electron detectors) and reconstruction methods. CryoEM has emerged recently as a powerful means of reconstructing the three-dimensional structure of complex nano-objects (proteins, viruses, engineered nanostructures) [448]. The technique consists of measuring a population of (randomly oriented) copies of the target structure (which have been immobilized in a vitrified matrix at cryogenic temperature). Algorithms have been developed to register the projection views of the individual objects, accumulating them into a single reconstruction view. At first glance, such techniques cannot be applied to the poorly-ordered motifs present in organic materials. However, with proper development, these techniques can be combined with recent developments in machine-learning (for clustering and sorting) to allow reoccurring local motifs to be identified and reconstructed. This represents a substantial development effort, but if successful, it would allow a

wide variety of semi-ordered materials to be studied, by reconstructing a catalogue of molecular motifs present in the material. Moreover, modern technique development in X-ray scattering and diffraction aims to go beyond the ensemble average and to also analyze fluctuations or variability in scattering signals (across time, across space, over angle, *etc.*). This analysis of higher-order moments of the data allows access to otherwise hidden signals, including inhomogeneities, defectivity, and hidden correlations. For instance, X-ray photon correlation spectroscopy (XPCS) can probe material dynamics[449], fluctuation scattering can reconstruct structures[450], angular correlations can resolve local motifs [451], variance methods can probe grain structures [452] and heterogeneity[453], and so on. There is enormous potential for further development of these approaches targeted towards functional organics, where they can be used to statistically resolve molecular motifs, reconstruct grain sizes/shapes, establish correlations between molecular- and micro-structure, and probe homogeneity.

Other bottlenecks arise because of the plethora of materials that exist and potentially can be produced in future, leading to numerous options with regard of materials choice for, *e.g.*, device fabrication, with an inconceivably high number of possible materials combinations to select from in particular for applications where, for instance, multicomponent systems are employed—such as OPVs. The only exception in this respect concerns dopants; there are still too few dopant molecules available to device physicists and designers. Furthermore, *n*-type doping remains extremely challenging and in general, the amount of free charges generated is small (~5%) although dopant ionization is quite efficient (>80%). Such low overall efficiency points to the fact that the charges remain localized near their counter-ion and have difficulty participating in the transport process. The mobility of the dopant in the active layer may contribute to these issues.

On the device front, arguably the highest-value challenge that still needs to be solved is to achieve *long-lifetime, 100%-internally efficient blue phosphorescent OLEDs*. While considerable advances have been made, as alluded to above, further progress is required to enable the full range of the promised applications. All organic and flexible electronic device platforms confront a number of remaining challenges including: to enable low cost manufacturing; to realize high precision patterning over very large flexible substrate sizes; to achieve long lifetimes even upon exposure to extreme conditions such as high temperatures and high humidities; to obtain high resistance to mechanical failure; and/or to advance sustainable routes to synthesis of very high performance materials. One largely unexplored area has been the exposure of organics and flexible materials platforms to very high energies and energy densities such as encountered in lasers, short-wavelength emitters, and blue- and UV-absorbing organic photodetectors, and their effect on the used materials systems and devices. Understanding the fundamental mechanisms leading to the degradation of the operating characteristics in the presence of high-energy excitations should lead to new chemistries and device architectures, while greatly extending our fundamental knowledge of this important class of optoelectronic materials.

There are also many future challenges and bottlenecks that we face for use of organic and flexible materials in *bioelectronics and biointegrated electronics* applications. Perhaps the most prominent challenge is related to the long-term stability of devices as they operate in challenging aqueous environments with high ionic strengths, complex biomolecules, and living cells. Implantable devices are impacted by mundane, yet critical issues such as robust sealing and encapsulation, packaging, inflammatory responses, infection, device failure, and finite battery lifetimes. Advances in *wearable devices* such as biosensors, for example, must address technical hurdles such as on-board power supplies, tissue adhesion, and low signal-to-noise ratios to convert raw data into knowledge about

one's health that can help inform decisions. The latter issues are aggravated as there is a striking lack of availability of new materials. For instance, in the area of mixed-conduction-based bioelectronics, most of the community uses blends of poly(3,4-ethylenedioxythiophene) and poly(styrene-sulphonate), *i.e.* PEDOT:PSS. This material presents several advantages, such as commercial availability, adequate performance and sufficient reproducibility. However, its complex and disordered microstructure has made it difficult to gain a fundamental understanding of the details of its working mechanism[454]. Furthermore, PEDOT:PSS is sold as a formulation and additives such as cross-linkers are often added. As a result, the material is very sensitive to processing conditions and experimental conditions lack generality. Finally, PEDOT:PSS is self-doped, therefore devices made with this material are "normally on" and draw current, which is not suitable for low-power solutions. In the case of *ion pumps*, a completely different set of limitations needs to be addressed. In these devices, ions have to drift through a polyelectrolyte (*e.g.* cations through a polyanion). As a result, ion pumps have been limited to small cations. Furthermore, the ionic resistance of the drift process often requires high voltages that are not compatible with physiological conditions. Hence, further materials discovery activities are required in this specific area of organic and flexible materials, which needs to be combined with the development of characterization techniques that allow measurements in complex environments—both contributing to the wider field.

5.5 Proposed approaches to address challenges

The organic and flexible electronics area is an inherently interdisciplinary field. As a consequence, the solution of the most intractable and high-value problems for organic and flexible materials and their science and technology platforms necessitates that we change how we do science in a fundamental way: *a combination of insights from physics, materials science, chemistry, electrical engineering and, in many cases, biology—bringing high-performance computational resources, theoretical approaches and top-of-the-range characterization techniques, generally only found in national laboratories —is required to address fundamental questions and technological challenges*. Relentless innovations in, for instance, materials design, thin-film processing, microfabrication and materials integration will underpin many prospective technologies. Thus, it can be expected that applying creative engineering approaches combined with distributed and cost-effective capabilities in materials synthesis, characterization and processing (*e.g.* 3D-printing, low-cost fabrication and patterning [352, 455], will catalyze solutions to many of the technical challenges highlighted above. Realizing this objective requires focused support by all stakeholders—in academia, industry, and government labs—many of whom have a vested interest in the advancement of organic and/or flexible technologies. This will ensure that the collection of capabilities available within the science-and-engineering toolbox can lead to ground-breaking fundamental knowledge, important innovations and future technologies: from highly emissive materials, true 'synthetic metals' (via doping of organic and flexible matter), to new architectures based on multi-component, multi-phase systems; inorganic/organic heterojunctions; stretchable materials; or systems with multiple and reversible functions. High-current electronics, new photonic- and quantum information systems, low-thermal budget devices, alternative application areas such as thermoelectrics and radiation-hard matter, and beyond, are also targets of great interest.

In order for such step-changes to be realized, however, we need to increase our understanding of relevant processing/structure/property-interrelations. In addition, we have to gain the capabilities to produce defect-free materials in a widely applicable manner (*incl.* single crystals over large areas and on any substrate); to fabricate more complex structures such as multilayers without restriction in composition, ingredients used (*e.g.*, solvents, substrates, additives), and to shape and

engineer systems with high stretchability and controlled form factors; advance stable, room temperature properties (optical, electronic, mechanical); to manufacture, *e.g.*, inorganic/organic junctions without need for lattice match in order to open an infinite materials palette; *etc.*

Many successes along those lines have been achieved already. In multilayers, modification of critical interfaces in organic electronic platforms with dipolar small molecules has been demonstrated to provide for control of surface free energy (wettability) and effective work function modification (controlling energetics). Certain molecular modifiers were also shown to control the orientation of the first layers within the active layer, thereby controlling dynamics of electron transfer. Addition of low concentrations of oxidizing (hole-doping) or reducing (electron-doping) agents was used in organic electronic platforms to control energetics, mitigate mid-gap (trap) states, and enhance device efficiency and stability. Similar approaches are beginning to be followed for thin-film nanocrystalline materials or 2D structures (such as 2D perovskites), even though it remains unclear, how effective they will be for these systems.

Further materials development is clearly required. To give an example in the area of biointegrated flexible electronics: Recent work has produced new materials that exhibit mixed conduction [373, 456, 457]—from homopolymers with backbones known for good electrical properties substituted with glycolated side-chains to allow facile ion penetration; to block copolymers where one block is conjugated while the second block is an ionic conductor [458]; to blends. The potential of these materials systems lies in the fact that they are intrinsic and well-defined (*i.e.*, they do not require additives) and therefore promise the dual advantage of offering performance complementary to that of PEDOT:PSS as well as the possibility to engage in systematic studies aimed at elucidating the interplay between ionic and electronic transport. Moreover, there is a need for new polyelectrolytes that would enable ion pumps capable of delivering larger-sized ions for therapeutic purposes. There is currently no clear vision on how to achieve this objective. Polyelectrolytes with large free volumes may be able to let bigger ions through. Alternatively, devising groups with chemical affinity specific to the desired ions could be another strategy.

In addition, further development of existing, and advancement of new characterization methods will be of outmost importance. One trend in modern technique development is to go beyond the ensemble average and to also analyze fluctuations or variability in scattering signals (across time, across space, over angle, *etc.*). This analysis of higher-order moments of the data allows access to otherwise hidden signals, including inhomogeneity, defects, and hidden correlations. For instance, XPCS (mentioned above) can probe material dynamics[449], fluctuation scattering can reconstruct structures[450], angular correlations can resolve local motifs[451], variance methods can probe grain structures [452] and heterogeneity[453], and so on. There is enormous potential for further development of these approaches targeted towards functional organic materials, where they can be used to statistically resolve molecular motifs, to reconstruct grain sizes/shapes, to establish correlations between molecular- and micro-structure, and to probe homogeneity.

Finally, the challenges on the *theoretical/computational* side remain numerous but their solution can bring high rewards. Here, it is critical that multi-pronged efforts focus on: *i)* gaining the ability to link the nano- and meso- scales (that is, the "local" morphology – molecular packing, mixing connecting networks) with the micro-scale (that is, the "global" morphology – domain size, domain purity, paracrystallinity); *ii)* rationalizing the impact of processing on both local and global morphologies; *iii)* establishing a description of charge and energy transport across a full-size

device based on actual morphologies, so as to relate morphology, processing, and performance; and *iv)* developing machine-learning tools efficiently tackling van der Waals-bound materials.

5.6 Future opportunities and directions

The ability to easily modify optoelectronic materials via changes in molecular chemistry in a seemingly infinite variety of ways provides a unique opportunity to exploit organics and other flexible materials for new applications that are inaccessible to conventional semiconductors. *Organics and many flexible materials platforms ultimately promise the ability to engineer "materials on demand" for a virtually endless range of purposes*. Fundamental challenges often lead to opportunities, as the example of research at the interface of electronic devices/applications and biology illustrates. Indeed, in the specific areas of bioelectronics and biointegrated electronics, many opportunities are motivated by the desire to understand and manipulate biological function using electronic devices. However, the tissue-biomaterials response compromises the long-term performance of almost any implantable electronic device ranging from futuristic brain-machine interfaces to commercially available implantable glucose sensors. Engineering biocompatible devices remains, thus, an important challenge that can be addressed, in part, by flexible and biointegrated electronics.

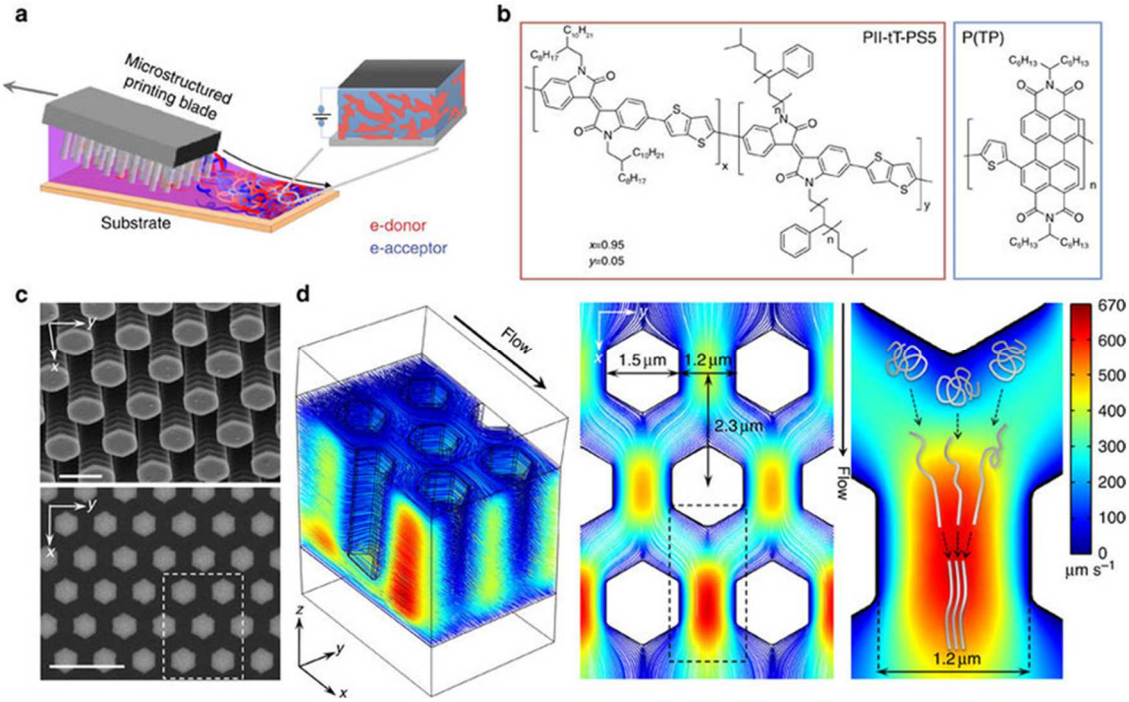

Figure 5.7. Example of processing OPV blends in well-defined micro-phase separated structures by manipulation of the fluid flow during solution printing using surface-structured printing blades. (a,b) Schematics of the method and he obtained resulting morphology. (c) Scanning electron micrographs of the printing blade, scale bar 2 mm (top), 5 mm (bottom). The white dotted line indicates the size of the simulation box in the xy plane. (d) Finite element simulation (stream-line representation) of the flow field between the surface-structured printing blade and the substrate. The simulated printing speed is 50 $\mu m \cdot s^{-1}$. The color scale of the fluid velocity is shown to the right. Figures adapted from Ref 423.

Broadening the view to the wider organic and flexible electronics area, opportunities are provided by new *materials discovery* activities: In addition to novel emitters, higher charge-carrier mobility materials, better ion-conductors, *etc.*, new *p*-type and *n*-type dopants that can have universal application (*i.e.*, that do not require *ad hoc* design for each new material/device), will have

tremendous impact. Also, advancing strong dopants that can induce large charge densities is a worthy goal: current doping densities are limited by phase separation and co-crystallization of dopant and semiconductor. Furthermore, pathways towards uniform incorporation of dopants and a high doping efficiency are needed.

Another important dimension of the organic and flexible electronics field is the many opportunities offered by advancements in innovative fabrication processes. From printing and coating (Figure. 5.7) to additive manufacturing, deposition techniques undergo rapid development, with clear potential impact for devices incorporating organic and flexible electronic materials. There exist increased capabilities to pattern them on stretchable substrates or substrates of complex shapes; however, realization of methods combining high resolution with high throughput is still challenging.

Regarding biointegrated devices, integration of electronics with ultracompliant materials such as hydrogels can be expected to have notable impact. *Hydrogel-based electronics* have the potential to seamlessly interface with electronically excitable tissues and organs such as the muscle, heart, and brain. In addition to fundamental studies to elucidate the mechanism for device encapsulation, there are also many fundamental questions with respect to signal transduction, *e.g.*, in the biomimetic area where protonic and ionic transport in many new kinds of functional biomaterials are of particular interest. Hence, *non-electronic charge transport*, when studied more formally by synthesizing and processing novel biomaterials into test structures, will lead to step changes. Expanding our ability to control the information flow of protons and ions in synthetic device architectures can contribute to our understanding of new transport mechanisms and serve as *in vitro* models to mimic the behavior of excitable tissues such as neurons [459]. Moreover, interfacing ionic and protonic devices to non-mammalian species such as bacteria and plants could catalyze new areas of research as well[460, 461]. New materials with better performance will allow one to make faster devices, possibly in the MHz regime. Higher conductivity will benefit the field of application of OECTs as well as thermoelectrics and electrochromics. There are opportunities to make ion pumps general-purpose devices, rather than being limited to small ions. This direction would be appealing as one could envision a pixelated drug delivery device entirely electronically controlled.

At the fundamental level, there are major opportunities in gaining fundamental insights far beyond the organic and flexible electronics area by developing *characterization methods* for studying phenomena such ion diffusion processes in mixed conductors or at important device interfaces. Combining methods such as thermal analysis, X-ray diffraction and neutron scattering, NMR spectroscopy and electron microscopy, would greatly enhance our knowledge of these processes. Further understanding of functional organic materials will be achieved by advances in measurement techniques targeting new manufacturing processes, such as additive manufacturing. In particular, X-ray scattering methods could be adapted to study the evolution of organics during deposition, by exploiting small focused X-ray beams, fast data acquisition, and a specialized in-situ-manufacturing setup designed for use at the beamline. Further, important insights will be gained by studying these materials under *operando* conditions—that is, while the materials are operating in a device context. *Operando measurements* go beyond *in situ* (studying materials in a particular environment), since they simulate real-work operating environments, and frequently include concomitant measurement of a functional property (battery charging, catalytic output, *etc.*). For organic and flexible materials, there is an opportunity to learn about material transformations that only occur under operating conditions—for instance when under the influence of an electric/magnetic field, or being irradiated with light. Such studies can shed light on transient

structures, non-equilibrium processes, and aging effects. Progress in this area will require the development of appropriate sample environments.

5.7 Connections to national initiatives and partnerships

This is truly an exciting time for the various communities who work to advance the design and implementation of organic and flexible devices. The most obvious initiatives poised to contribute to these fields is the Materials Genome project and the National NanoInfrastructure Network. Industry has a very substantial stake in OLEDs and solar energy generation and hence there are ready partners for collaborations in these areas. National laboratories should be key partners in the development of improved measurement techniques focused on semi-ordered materials. The Department of Energy (DoE) user facilities have advanced capabilities in electron microscopy and nanomaterials characterization (within the Nanoscale Science Research Centers, NSRCs) and X-ray science (within the synchrotron facilities); neutron experiments are available both through the DoE and the National Institute of Standards and Technology (NIST). These user facilities are ready and eager to engage, and represent a world-leading resource that should be aggressively leveraged. These facilities should get involved both through their user programs, and as collaborators in the development of frontier measurement capabilities.

National user facilities can also play a role in 'big data' efforts; that is, the exploitation of data mining and machine-learning methods for the analysis of scientific data. For such efforts to succeed, improved data sharing and common standards must be developed. Facilities can play a role here, coordinating efforts and developing common software. However, to succeed, such efforts also require emphasis from funders, both through mandates to researchers, and by funding efforts to coordinate and develop common standards/software. One of the key end-goals for such big data efforts is the development of autonomous experiments[462, 463], where computer-guidance of experimentation itself can maximize the utility of valuable experiment time. Here again, facilities can play a key role, but this will require deep engagement from the academic community to guide developments and provide compelling scientific problems.

Another highly prominent example of commitment from a federal level is that of the Brain Research through Advancing Innovative Neurotechnologies (BRAIN) initiative (see: National Institutes of Health (NIH); https://www.braininitiative.nih.gov/), which aims to revolutionize our understanding of the brain. The BRAIN initiative has many important synergies with technical advances in flexible and biointegrated electronics [464]. The use of mixed conductors for neural probes falls within this initiative. One challenge is to introduce the mechanics community, which is used to its tools, such as metallic probes, to a new materials set. Furthermore, partnerships with National Laboratories, which could become "one-stop shops" for characterization through their user facilities, is desirable here as well.

As mentioned earlier, flexible and biointegrated electronics can contribute meaningfully to 3 of the 14 grand challenges set forth by the US National Academy of Engineering (NAE). Existing public-private partnerships such as NextFlex (The Flexible Hybrid Electronics Manufacturing Innovation Institute; https://www.nextflex.us/) can also provide resources and collaborative opportunities to advance flexible electronics through public-private partnerships[465]. Private corporations have also invested heavily in recent years to advance progress in bioelectronics. GlaskoSmithKline and Google (Verily) have been active partners in many academic projects aimed at accelerating technology related to electroceuticals with relatively short project timelines of 5–10 years. In the area of brain-machine interfaces, both large cap tech companies (*e.g.*, Facebook) and newly formed private corporations (*e.g.*, Bryan Johnson's Kernel and Elon Musk's

NeuralLink) have initiated numerous projects with more ambitious goals, riskier technology, and longer timelines of >10 years. Taken together, many stakeholders have identified the enormous potential to improve health and quality of life that can be unlocked through organic and flexible materials and devices that seamlessly meld electronics with the human body.

6 Metamaterials

6.1 Promise and potential impact

Metamaterials are artificial composites with structural size much smaller than the light wavelength, and they exhibit various extraordinary properties not achievable in natural single-phase materials, such as negative refraction [466], hyperbolic dispersion [467], and optical magnetism [468]. Recent innovation and discovery in science and technology of metamaterials [469-471], particularly at the nano- and microscale, have undoubtedly opened doors to new venues for unprecedented control of electromagnetic waves, acoustic signals, and thermal emission distribution. For example, metamaterials have found various applications for subwavelength imaging [472], superlensing [473], biological sensing [474], invisibility cloaking [475, 476], and several other applications of broad technological interest. Yet, as we discuss in this document, important challenges need to be addressed to advance this technology for broad societal impact.

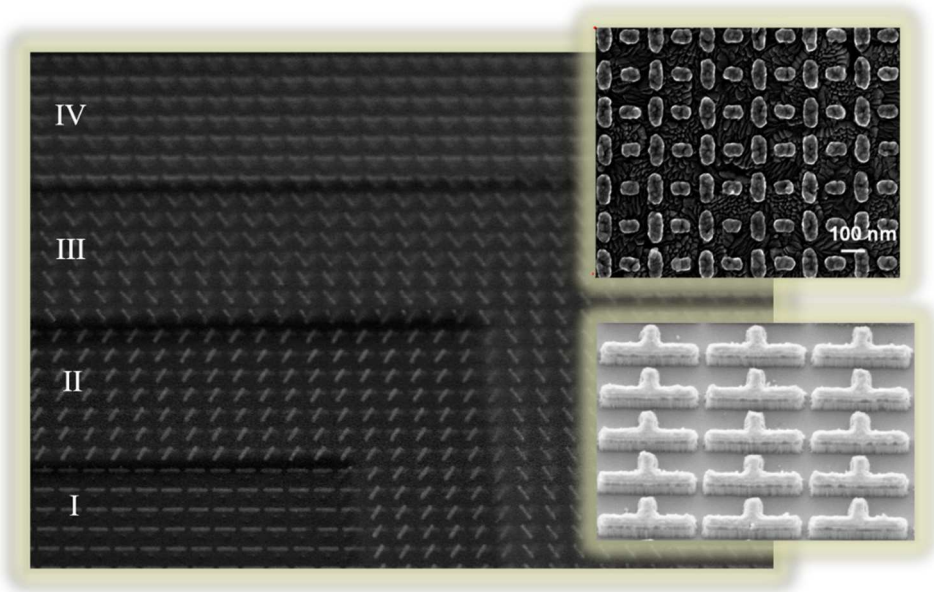

Figure 6.1 Examples of optical metamaterials realized with conventional lithographic techniques[7].

At optical frequencies, most metamaterials are composed of nanostructured noble metals (e.g., gold and silver) with subwavelength size embedded in a dielectric matrix, which present novel platforms for light-matter interactions. A few examples of optical metamaterials are shown in Figure. 6.1. In these samples, the microstructures of the artificial materials are responsible for their unique emergent properties, significantly different from those of their individual constituents. In these cases, they exploit plasmonic resonances, which are collective excitations of electrons residing at the interface between metal and dielectrics or free space [477]. We can engineer the

collective response of these resonant particles by tailoring their geometry, orientation, alignment and density throughout the different layers of nanoparticles composing the metamaterial, in order to realize a bulk material with strong, localized light–matter interactions that can be homogenized and described as a bulk material with emergent properties distinct from those of the constituent materials. Based on this paradigm, we can change the way in which electromagnetic waves interact with materials, propagate through them, diffract, scatter, reflect, or refract.

Early research on metamaterials was driven by the opportunity to engineer unusual values of their constitutive parameters, such as a bulk index of refraction with a negative real part, which, as mentioned above, has been shown to enable the possibility of bending waves in unusual directions and realize flat lenses with no aberrations and superior resolutions, or cloaking devices that reroute the impinging waves to hide a given region of space from the background. These ideas have been inspiring researchers worldwide, but so far we have not seen the expected major impact on practical devices and technology. It is clear that significant efforts in material science research, guided by parallel advances in electromagnetic engineering, may provide exciting breakthroughs for metamaterials, with the prospect of revolutionizing several fields of research and technology.

6.2 Recent breakthroughs

Some exciting breakthroughs have occurred in metamaterials research in the last few years. The common goal is to endow the designer material paradigm with new degrees of freedom that may challenge some of the inherent limitations of current metamaterials. For instance, hybrid metamaterials and metasurfaces that combine different phenomena over the same material platform, as in the case of optomechanics or acoustoelectric phenomena, are being explored. Tremendous research efforts are being devoted to develop ideal methods to synthesize these nanoscale metamaterials over large scale and at low cost. To date, various methods have been implemented, which mostly can be divided into two categories: bottom-up and top-down. Promising bottom up methods include block copolymer self-assembly [478], template-assisted electroplating [479], DNA-mediated self-assembly of nanoparticles [480], as well as the recently developed self-assembled hybrid materials by one-step pulsed laser deposition (PLD) technique [454]. In parallel, top-down methods involve direct laser writing [481] stacked electron-beam lithography [482]. and membrane projection lithography [483]. These methods have their own advantages and disadvantages. For example, template-assisted electroplating is simple and cost effective, however complicated and challenging for scale-up and device integration; laser writing and e-beam lithography related methods are ideal for feature size control at the nanoscale (in the range of few tens and 100s of nanometers). However, they are expensive, time consuming and sometimes lead to material damages.

One representative example of bottom-up methods is the recently developed self-assembly growth of oxide-oxide and oxide-metal hybrid materials by the one-step PLD technique. [484] Metal-oxide hybrid materials systems have been demonstrated by other methods such as core shell particles, alumina templated metallic nanowires, and FIB grown Ag in alumina templates. However direct thin growth of such oxide-metal hybrid materials has been considered very challenging due to the vastly different surface energy and growth kinetics of metal and oxide, as well as the possible inter-diffusion. Very recently, $BaTiO_3$ (BTO)-Au nanocomposite thin film with Au nanopillar embedded in BTO matrix has been successfully demonstrated by Li *et al.*. [484] Au nanopillars with

high epitaxial quality and very small diameters (average diameter ~20 nm) have been achieved, which is in the subwavelength regime. By both simulation and experimental measurements, interesting optical properties have been explored. For instance, resonant surface plasmon polaritons resulted from Au nanopillars are observed in the absorbance spectrum. In addition, anisotropic optical response was demonstrated via angular dependent and polarization resolved reflectivity measurements, which have been further supported by full-wave simulations and effective medium theory.

In parallel, colloidal synthesis has been used to create subwavelength (e.g., 50 nm – 500 nm), Au and Ag nanostructures, allowing fundamental studies of their size- and shape-dependent optical properties [485, 486], and investigation of their applications for medical diagnostics and therapeutics [487] and as building blocks of optical meta-surfaces and materials [276, 411, 488]. These approaches to large-scale self-assembled metamaterials, as shown in Figure 6.2, appear to be important breakthroughs to realize large-area optical metamaterials with low cost and high speeds. In this context, printing and nanoimprinting have enabled the scaling of metamaterial fabrication to large, greater than centimeter areas [489, 490].

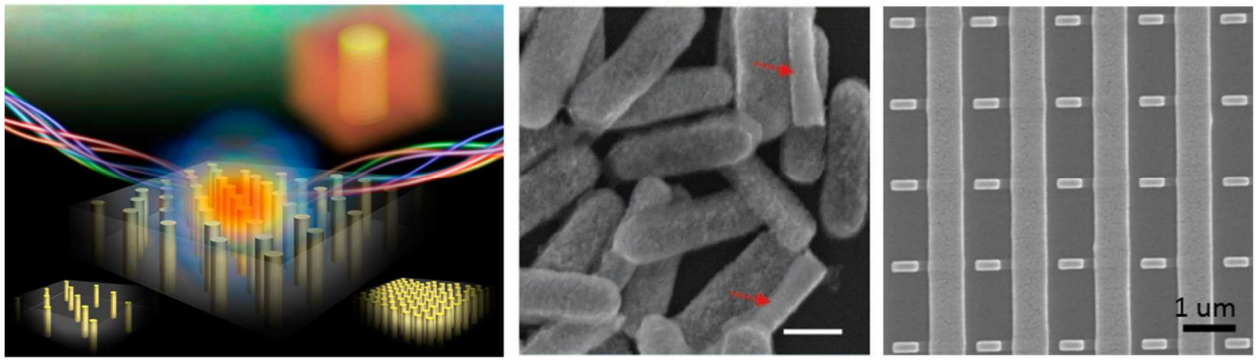

Figure 6.2. Examples of self-assembled optical metamaterials realized with breakthroughs in nanofabrication techniques. Figures adapted from Ref. 484, 515, and 489.

In addition, plasmonic materials have recently been expanded to include Al, to create UV plasmonics [491], low-carrier density metallic nitrides [492], and highly-doped semiconducting oxides [493-495] that are operative in the near- to mid-infrared range. The development of alternative constituent materials at optical frequencies, in particular doped oxides, nitrides [496-498] and high index dielectrics [499-502] Doped oxides and nitrides provide for lower loss plasmonic resonances in the infrared and near-infrared and can be tolerant to high temperatures. Dielectric metamaterials on the other hand, utilize Mie resonances in high index particles and can virtually eliminate absorption loss. Dielectric resonators can exhibit both electric and magnetic resonances in relatively simple geometries (spheres, cylinders, etc.) alleviating some of the fabrication challenges associated with metallic resonators.

Another breakthrough in materials design has consisted of creating subwavelength plasmonic structures by hierarchical design from compositionally-tailored nanoscale (~2-20 nm) building blocks. Tuning the number and arrangement of nanocrystals [503-505] and their inter-particle distance (e.g., through ligand chemistry) [506] enable control over the optical properties of materials, for example the energy and strength of resonances in weakly-coupled nanocrystal assemblies. The effective dielectric function is tunable through an insulator-to-metal transition as the coupling

strength between nanocrystals is increased. Assembly of two- or three-types of nanocrystals enables the realization of materials that mix materials' functions. For example, the co-assembly of plasmonic and luminescent nanocrystals provides for enhanced luminescence [507, 508] and for gain to compensate plasmonic loss. [493] Exciting opportunities offered by active metamaterials to overcome some of the challenges of conventional metamaterial approaches, especially in relation to bandwidth and efficiency constraints, have been discussed in several recent papers on parity-time symmetric metamaterials [509-514]. Mixing plasmonic and magnetic nanocrystals in assemblies enables exciting opportunities for magnetically-switchable optical responses [515]. Other important breakthroughs have occurred in ultrathin *metasurfaces,* [411, 516, 517] leading to many new insights into how metamaterial concepts can be applied in planar geometry, leading to ultrathin optical elements such as lenses [518, 519] and polarization optics [520-522].

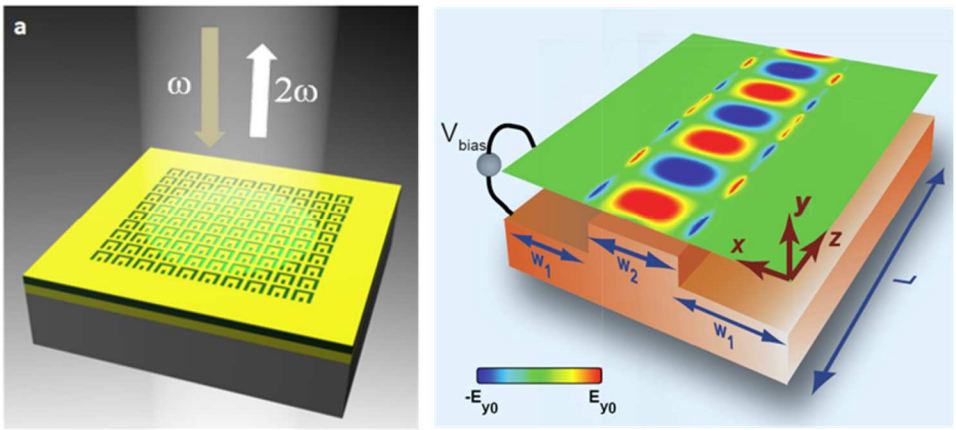

Figure 6.3 Examples of metamaterials integrated with multi-quantum well materials for giant nonlinear enhancements, and with 2D materials. Figure adapted from Ref. 525 and 523.

In the context of material science and the interests of the other thrusts of this workshop, metamaterials have also recently benefitted from the integration with graphene [523, 524], other 2D materials, and quantum-engineered substrates [525-530] (Figure 6.3). Graphene metamaterials exhibit the ability to guide highly confined EM waves and fields, and thus can act as platforms for thinnest possible optical devices, such as one-atom-thick optical waveguides, cavities, splitters, etc. in the mid IR wavelength regimes [523, 524]. Significant research activities in 2D materials in recent years provide promising possibilities for such few-atom-thick optical devices in the future. [531, 532] Multi-quantum well metamaterials, in parallel, have enabled unprecedented access to nonlinearities, opening an entirely new paradigm for nonlinear optics, including the possibility of achieving large efficiency in deeply subwavelength footprints. When combined with plasmonic nanostructures, suitably tailored to couple and enhance the impinging radiation and to out-couple the generated currents to free-space radiation, these quantum engineered metamaterials can realize unprecedented levels of optical nonlinearities, localized in deeply subwavelength volumes [525-530]. These studies extend the metamaterial concepts to tailor strong nonlinear interactions in various forms.

Finally, another exciting breakthrough in metamaterials has been offered by the paradigm of extreme-parameter metamaterials [533, 534]. In such structures, owing to the effective refractive index being near zero, unique and exciting properties in the wave mechanism and quantum optics are exhibited [535, 536]. Various phenomena such as photonic doping [537], super-coupling [533], electric

levitation [538], effective "perfect magnetic conductors" [537], extended Purcell effect [539], harnessing vacuum fluctuations [540], geometry-independent cavities [541], and quantum emitters behavior [542] are resulted from wave interaction with zero index metamaterials.

6.3 Challenges and proposed approaches

There are a few reasons behind the slow transition of these exciting basic research advances in the area of metamaterials to practical technology. Importantly, metamaterials typically require subwavelength resonant structures, experience significant loss, and suffer from stringent limits on the overall bandwidth of operation. In addition, previously demonstrated metamaterials are typically time-invariant, and therefore, lack reconfigurability. Finally, fabrication challenges have limited their overall applicability over large scales and with reduced costs.

Applications of plasmonic building blocks in metamaterials require control of their optical function. [496] However, the loss of noble metals in the visible or of oxides in the near- to mid-infrared, is too large for realizing metamaterials with designed index, e.g. epsilon near zero (ENZ) materials. Methods to arbitrarily design the function of plasmonic materials remains a challenge both experimentally and through simulation. While colloidal nanocrystals may be used as plasmonic building blocks, residual inhomogeneities in nanocrystal size, shape, and composition give rise to variations in their optical response. Nanocrystal assembly is also typically driven by entropic terms and gives rise to close-packed arrangements. Methods to define open and arbitrary architectures are needed to design optical responses at will. Often classical models are used to describe the optical dielectric function of materials. However, for nanoscale particles the optical response is unlike that of the bulk. At short interparticle separations typically found in materials assembled from colloidal nanocrystals, quantum mechanical models are needed to capture their coupling and predict their optical functions [543].

The design and synthesis of multimaterial architectures is still in its infancy. Multimaterial architectures present an opportunity to couple uncommon electronic, photonic, magnetic, mechanical, thermal materials properties and to realize reconfigurable materials and a new suite of functional devices. Metamaterials and chiral plasmonic materials [544] require three-dimensional fabrication of plasmonic nanostructures. While electron-beam lithography allows for high-resolution alignment of sequentially fabricated layers, large-area techniques such as printing/imprinting technologies have poor, micron scale alignment. Metasurfaces may be designed for a number of applications to avoid three-dimensional fabrication. But for a number of applications large-area fabrication of three-dimensional structures are needed.

Much effort is currently focused on dynamically reconfigurable metamaterials using a wide variety of techniques including phase change materials [545, 546], liquid crystals [547, 548], carrier injection [549, 550], mechanical actuation [551], and nonlinearity [552]. However, dynamic control remains a challenging task at optical frequencies as dynamic refractive index contrast is usually small while larger contrast often comes at the cost of slow operating speed, absorption loss, or high input powers. Many challenges remain in this space on the fundamental materials, metamaterial design, and electronic integration. It should also be noted that both fast and slow temporal responses are of interest. While applications such as LIDAR and optical communications require ultrafast operation, in applications such as tunable lenses speed is a secondary concern compared to energy efficiency, dynamic contrast, and cost. Ultimately, this area of research can benefit from both

fundamental materials (CMP) and device level (EPD) developments as well as advances in epitaxial, van der Waals, and phase change materials.

Another key challenge is integration of metamaterials with high quality crystalline materials such as semiconductors, nonlinear materials, graphene and van der Waals materials. While past work has been performed in all of these cases, improvements still need to be made in coupling two materials as well as exploring the additional engineering freedom provided through metamaterial design. This area would also benefit from more work on integration with electrical control and readout schemes.

While metasurfaces have provided a way for creating ultrathin optics there are limits with regards to their bandwidth, nonlinearity, polarization rotation, etc. A remaining challenge is how to create more complex and functional meta-optics based on multiple metasurface layers. This approach is similar to what is happening in the van der Waals material community wherein new functionality may be derived through stacking of 2D materials. Creating multilayer meta-optical materials would provide additional freedom in controlling the nonlinear response or provide a means for improving the bandwidth. One challenge is that these devices are difficult to design as full-wave simulations become unpractical as the domain size, or number of layers, grows. More efficient and informative design techniques are needed here. Multilayer optics are also difficult to fabricate as the geometries required for each layer may be significantly different. This may be an area that can benefit from integration with van der Waals materials as well as advances in manufacturing metamaterials at large scales and on flexible substrates.

In the context of zero-index metamaterials, materials such as SiC are good examples of mid IR, low-loss ENZ materials suitable for applications. [553] In the near IR and visible domains, ENZ materials with lower loss are desirable and needed. In addition, while photonic crystals with Dirac dispersion and accidental degeneracy [554] are excellent synthetic low-loss platforms behaving as effective low-loss ENZ and zero index materials, it will still be desirable to have natural very-low-loss optical materials with ENZ properties in the visible wavelengths. In this context, it is not only important to address the need for further reduction of the level of loss in materials, but also realize material substrates with large nonlinearity and large index of refraction, ideally with the possibility for modulation. An order of magnitude improvement in any of these material properties would open up a completely new playground for metamaterial functionalities.

Finally, further work is needed in the following areas: (1) precise control of the dimension and shape of these nanostructured metallic inclusions; (2) versatile material selections to meet the specific needs of optical functionalities. (3) ordering of the nanostructures; ordering of the nanostructures directly relates to the optical properties and functionalities required by optical devices and components on chip. Thus, such control is needed for the controlled light matter interactions; (4) cost-effective and scalable fabrication methods for metamaterials are very critical for future applications. (5) integration with other device components on chips.

6. 4 Future opportunities and directions

In the near future, exciting opportunities will stem from research in materials science and metamaterials, including the following directions.

Metamaterials for information processing with ultralow energy: Use of optics in signal processing has a long history. However, in recent years the idea of metamaterials for performing mathematical operations and information processing [555, 556] has brought a new mindset and a novel application of wave interaction with metamaterials, and has ignited the interest in near-zero-energy analog computing and processing. Such "informatic metamaterials" can provide smaller platforms for optical analog parallel processing at the micro- and nanoscale with ultralow energy. Needless to say, there are challenges ahead, which include: (1) ability to tune and change the platform in real time, thus allowing "programmable computing", (2) low loss materials in order to allow possible multi-stage cascading of such structures, (3) integration of such material structures with the rest of the computing platforms such as the electronic parts; and (4) storage of optical information.

Optical metatronics: The concept of optical metatronics, i.e., optical nanocircuitry inspired by metamaterials, has provided a new paradigm for connecting many aspects of electronics with photonics [557-559]. The properly designed nanostructures that behave as optical lumped nanocircuits allow the two-way exchange of ideas between the electronics and photonics. This concept is now being expanded into quantum optics [560]. There are challenges such as (1) proper spatial placement of nanoparticles on the platforms, (2) real-time ultrafast change of the material parameters in order to endow fast tunability and programability of such optical circuit elements.

Temporal and spatio-temporal control of waves in metamaterials: It is well known that spatial inhomogeneity in material platforms can provide useful features in controlling waves in structures. By analogy, temporal variation of material parameters can bring added "knobs" in manipulating and tailoring light-matter interaction. This feature has been utilized to induce nonreciprocity for acoustic, optical and electronic signals [561-564]. Other interesting wave phenomena have also been explored in spatio-temporal metamaterials. As mentioned above, challenges include: (1) speed and depth of temporal modulations for low-Q systems, (2) spatial and temporal variations with different rates at different locations of the material platforms, and (3) low energy modulation, just to name a few.

6.5 Connections to national initiatives and partnership

As evident in these discussions, the field of metamaterials is inherently multi-disciplinary, and it offers a unique platform to connect material science with broader national initiatives and partnerships with larger funding opportunities, such as EFRI, MURI, and MRSEC. DoD has been very interested in several of these recent advances. Thus, there is a clear opportunity to leverage significant funding to broaden material science research efforts by bridging these initiatives and applications. Also the National Photonics Initiative offers an important opportunity to connect with industry.

7 Industry Perspectives

Basic material research lays the foundation for technology innovations that eventually lead to commercial products. The semiconductor industry has not only significantly advanced research in electronic and photonic materials (EPMs) but also greatly benefited from scientific discoveries in novel materials, characterization methods, and fabrication techniques. This section will highlight some progress in EPM areas funded by the semiconductor industry, especially through the Semiconductor Research Corporation (SRC). SRC is by no means the only industry research

consortium; however, for 35 years SRC has provided a successful platform for public-private research collaboration and played an important role in funding basic research to advance semiconductor technologies. Examples of research achievements and the strategic research directions in SRC programs help to illustrate the industry perspectives on EPM research.

CMOS scaling guided by the Moore's Law has sustained exponential growth of transistor density on chip over several decades and enabled increasingly powerful microprocessors that support the electronics, computing, software, and defense industries with market value at trillions of dollars. Although CMOS transistors can still be scaled down in size and operated at higher frequency, circuit frequency increase has stalled since early 2000 due to increasing on-chip power density and heat dissipation. The difficulty to scale down transistor threshold voltage and supply voltage as well as the increase of passive power dissipation due to inevitable leakage have all contributed to the "energy crisis" on chip. This critical challenge has motivated the semiconductor industry to explore low-power devices beyond CMOS transistors. In collaboration with NSF and NIST, SRC launched the Nanoelectronics Research Initiative (NRI) program in 2006 to explore low-power switches that can outperform CMOS transistors in critical applications. The discussions in this section are drawn from research activities performed in the NRI program.

7. 1 Recent electronic and photonic material breakthroughs

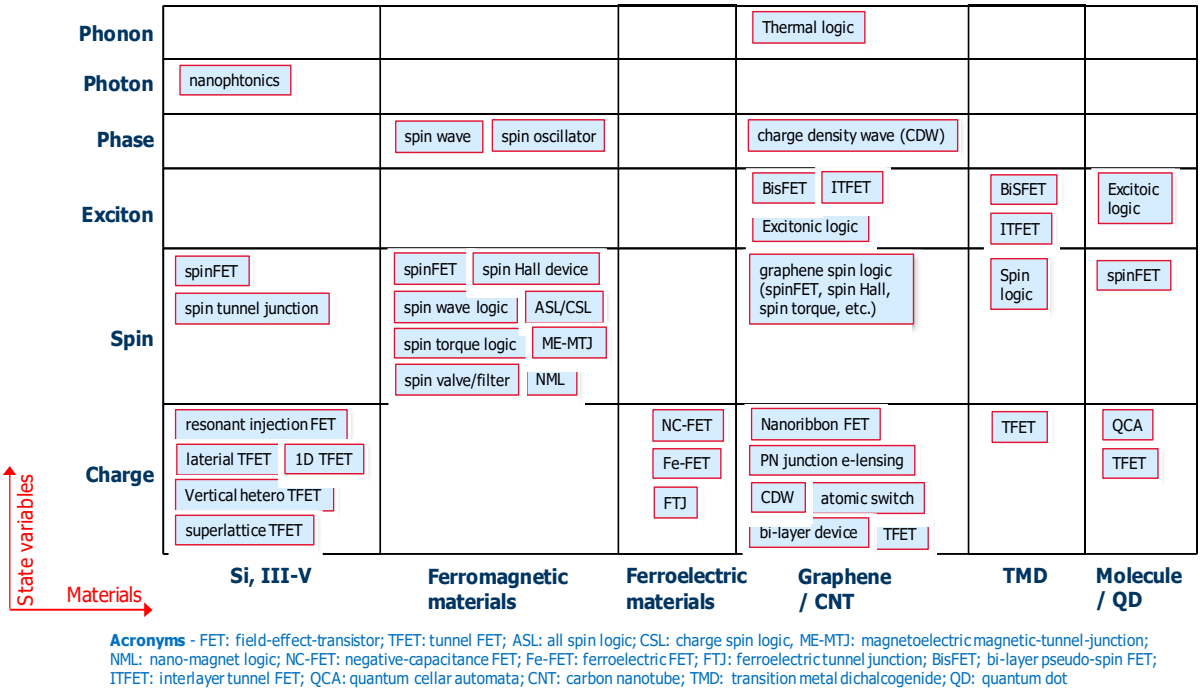

Figure 7.1. Beyond-CMOS devices explored in the Nanoelectronics Research Initiative (NRI), categorized by their state variables and materials used to make these devices.

NRI explored a wide range beyond-CMOS devices based on non-charge state variables (e.g., spin, photon), novel switching mechanisms (e.g., phase transition, collective effect), and unconventional materials and structures (e.g., functional oxides, van der Waals (vdW) materials, multiferroic materials). CMOS transistors can continue to be improved by adopting new materials (e.g., high-mobility channel materials) and device structures (e.g., 3D vertical, gate-all-around).

However, the thermionic emission mechanism in field-effect-transistor (FET) causes a minimum sub-threshold slope (60mV/dec), limiting how small the applied voltage (V_{dd}) can be for a target on/off current ratio. To achieve significantly lower sub-threshold slope and V_{dd}, it is necessary to exploit novel device mechanisms (e.g., band-to-band tunneling) and even devices based on the modulation of non-charge state variable. Emerging devices can be categorized as "CMOS extension" (based on conventional FET mechanism but improved with new materials and structures) and "beyond-CMOS" (based on novel mechanisms manipulating either charge or non-charge state variables). The novel mechanisms of beyond-CMOS devices often require new materials for implementation. Therefore, significant resource in NRI has been spent on studying new materials, fabricating and integrating them in new devices, and characterizing their unique properties.

Figure 7.1 summarizes the large variety of devices explored in NRI based on their state variable and the materials used to build them. Industry has many years of experience of processing conventional semiconductors (Si and III-V); therefore, novel devices based on Si or III-V would have significant advantages in potential industry adoption. Ferromagnetic and ferroelectric materials are the foundation for spintronic devices and nonvolatile electronic devices. Some of these materials have been integrated in CMOS process and commercial products (e.g., MRAM, FeRAM). Carbon materials, including carbon nanotube (CNT) and graphene, are considered one of the most promising candidates after Si and are highlighted in the ITRS Roadmap for emerging devices.[565] Devices based on various state variables have been implemented on CNT and graphene. Challenges still exist on wafer-scale growth and processing of carbon materials, as well as the control of material properties (e.g. chirality of CNT) required to achieve sufficient device yield. The rise of other 2D materials beyond graphene provides a much wider space to explore new device physics in these atomically thin material platforms. The heterostructures of these 2D materials utilize their versatile properties for novel device applications and are promising for 3D stackable device architectures. The success of CMOS scaling has also driven the industry to explore the "ultimately scaled" materials and device structures, e.g., molecules, DNA, quantum dots. These materials and structures are exploited not only for their extremely small size (and potentially high device density) but also new phenomena emerging at low dimension (e.g., Coulomb blockade) for device applications.

Some important material research achievements in the NRI program are worth mentioning:

1. The invention of Cu-based large-scale CVD growth of graphene[233]. This breakthrough was achieved through academia-industry collaboration within NRI and has been adopted worldwide by both academic researchers and industry for commercialization.
2. The demonstration of electrical switching of boundary magnetization in Cr_2O_3 useful for low-power field-switching of nonvolatile magnetic memory and logic devices[566].
3. The demonstration of novel physics in 2D materials including graphene, e.g., the proof of electron optics in graphene PN junction[567], room temperature exciton in heterostructures of 2D materials[568].
4. The invention of new device concepts that stimulate interests in material research, e.g., negative-capacitance FET which has put ferroelectric doped HfO_2 at the focus of low-power device research[569].

Other SRC programs, Global Research Collaboration (GRC) and Semiconductor Technology Advanced Research Network (STARnet), have also dedicated significant resource in material research and achieved important breakthroughs, for examples:

1. The invention of black phosphorus as a new 2D material with direct band gap and great potential for electronic and optical applications. [570]
2. The invention of growth techniques for vertical InGaAs and InGaSb nanowires to enable asymmetric source/drain and gate-all-around MOSFET structures. [571]
3. The utilization of graphene as a barrier layer for Cu interconnect with improved reliability and electrical/thermal conductivities. [464]

SRC researchers also developed a comprehensive material benchmarking database with the collection of reported material parameters, processing methods, and key properties for device applications. Starting from a material framework for beyond-CMOS devices, [465] researchers in the NRI and STARnet programs have compiled a extensive multi-scale material database.[572] The SRC material database covers 2D materials and their heterostructures, solid-state polymers, nitrides, phase-change materials (e.g., VO_2), ferromagnetic materials, ferroelectric materials, multiferroic materials, topological insulators, etc.

7. 2 Key challenges in EPM research from industry perspectives

The industry's interest in new materials is driven by *applications*, which is also a key challenge for some novel materials. Unique properties and interesting physical phenomena enabled by new materials may be utilized to build new devices or develop new methods for processing and integration. However, there are significant barriers and challenges from the basic feasibility to industry adoption, requiring years of R&D and investment. Although basic feasibility of a novel material for an application is determined by its intrinsic properties, extrinsic factors (e.g., defects, parasitic, contacts) often dominate the performance of the actual device. Promising applications of a new material also need to be benchmarked against incumbent technologies and alternative candidates. Only with truly significant improvement in performance and efficiency or reduction in cost will a new application gain traction.

The second major challenge of novel materials is *scalable manufacturing*. Wafer-scale material preparation and processing methods need to be developed to bring any new materials from lab to fab. Quality, yield, and throughput are all important for manufacturable materials. For example, the exciting prospect of 2D materials for novel devices will remain as laboratory activities instead of industrial reality, without wafer-scale material growth, patterning, and processing methods. Material quality and manufacturing requirements also depend on applications. For example, 2D materials for CMOS applications would require significantly higher material quality and fabrication precision than those for applications in display or flexible electronics. Control of defects and contamination is also challenging with new materials.

As CMOS technology dominates the semiconductor industry and will continue so in the foreseeable future, *CMOS compatibility* is a key challenge (or requirement) for any new materials and devices. Materials need to be processed with CMOS tools and be compatible with standard materials used in CMOS devices and architectures. Materials that can be grown on Si substrate with high-quality and yield would be able to utilize the extensive manufacturing capabilities developed for Si, which is still a challenge for III-V materials. New materials also need to meet CMOS processing requirements (e.g., thermal budget).

From the industry perspective, benchmarking provides important assessment of the large variety of materials and can be used as a guidance to focus resources on the most promising candidates. *Material benchmarking* should be developed and adopted by both academic and industry researchers. For example, various vdW materials and their heterostructures call for uniform benchmarking methods and metrics for comparison.[573]

7.3 Recommendations for NSF EPM program

Electronic and photonic material research plays vital roles for identifying new frontiers for industry exploration and applications. The NSF EPM program, similar to other programs focusing on fundamental science, faces funding challenges. Leveraging industry support may provide opportunities to more effectively channel scientific breakthroughs into industry R&D, which may eventually lead to products with substantial societal impact and more resources for research. At the same time, the semiconductor industry today is more eager to explore basic research of novel materials to address the challenges at the end of CMOS scaling. Therefore, the first recommendation for the EPM program is *to develop more programs for industry collaboration*. There are multiple mechanisms to collaborate with industry in EPM programs, including co-funding university research, university-industry joint R&D, industry participation in EPM activities (e.g., NSF panels and workshops), industry internship for EPM funded students, EPM-industry joint studies and reports to influence research strategies and resource allocation, etc.

A group of experts from leading semiconductor, computing, and defense companies have developed an industry vision and guide for semiconductor research opportunities at the end of 2016.[574] Some *important material research directions* have been suggested by this industry working group.

- Basic research on growth/synthesis methods of new materials with some consideration given to substrate properties and interactions. Explore novel material properties at reduced dimension and new state variables that emerge from dimensional scaling. Research to quantify transitions from uncorrelated many body to correlated few body and beyond. Explore state variables, e.g., quantized charge, neutral or ionized excited state, or nuclear state, relative to chemical and physical structure and dimension. Studies to characterize the range (temperature, length, time, electrical bias, etc.) over which a state variable can be maintained.
- Materials for beyond-CMOS devices: (1) low-power devices to improve von Neumann computing; (2) novel devices to enable non-von Neumann computing
- Materials related to devices and applications for internet-of-things (IoT), including ultra-low power devices, sensors, flexible electronics, energy harvesting and storage, THz communication among others
- Materials for 3D integration: deposition, growth or placement of dissimilar materials and hetero-structures with low defect density; materials for high-density, fine-grained, monolithic 3D systems
- Interconnect materials: sub-10nm electrical interconnect materials, barriers, low-dimension materials with novel transmission properties, photonic materials
- Novel materials for nanofabrication: materials for atomic scale precision deposition and self assembly; photolithographic and patterning materials; interface-determined functionality; materials for etching and surface planarization
- Advanced material characterization and metrology techniques
- Atomistic and multi-scale modeling techniques for material properties, dynamics, defects, interface, etc; modeling tools for experimental calibration and material screening for potential applications

From industry perspectives, these material research directions will have direct impact on the semiconductor and electronics industry. Breakthroughs in the fundamental science of electronic and photonic materials may lead to unprecedented technology innovations and opportunities to reboot the maturing semiconductor industry.

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