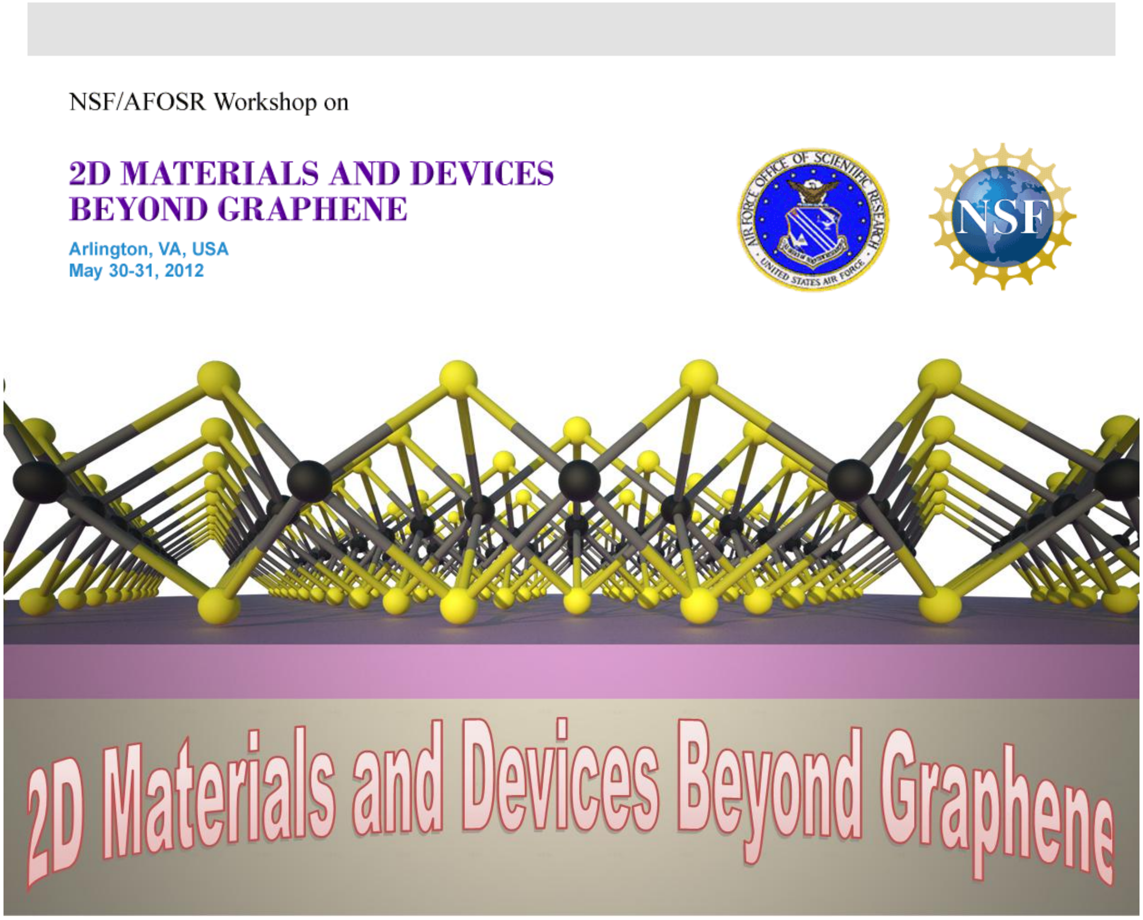
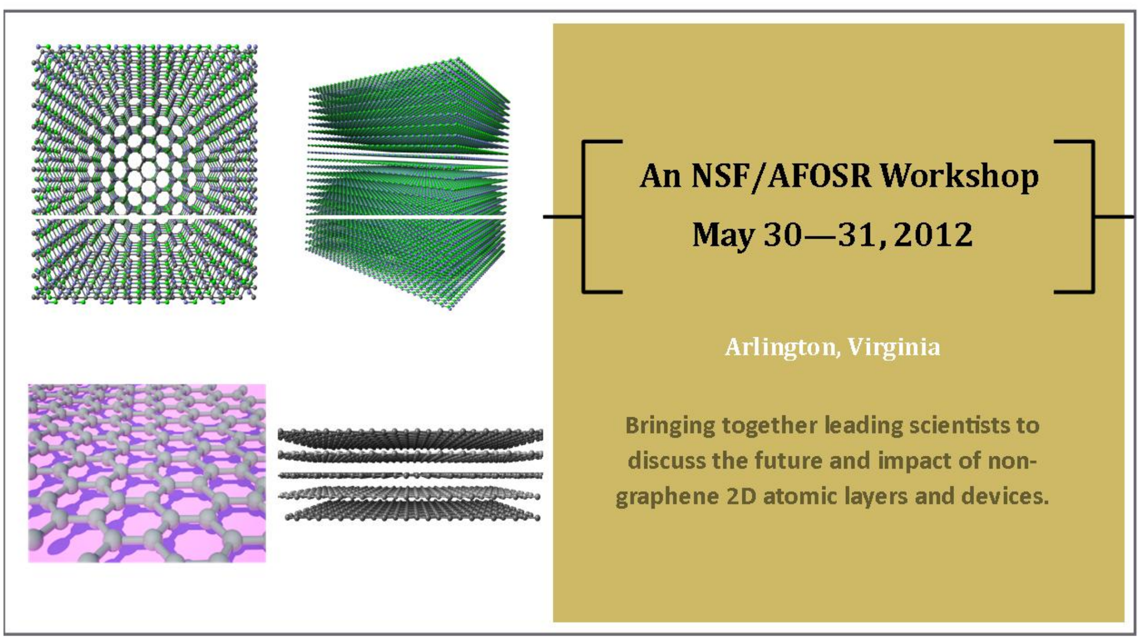
Final Report – NSF AFOSR Workshop May 30 – 31, 2012

http://nsf2dworkshop.rice.edu/





2D Materials and Devices Beyond Graphene

An NSF/AFOSR Sponsored Workshop

Workshop Chair, Co-organizers, Discussion Leaders

Workshop Chairs

Pulickel M. Ajayan, Chair (Rice University)

Jun Lou, Co-Chair (Rice University)

Co-organizers

Anupama Kaul, Program Director, National Science Foundation

Z. Charles Ying, Program Director, National Science Foundation

James C. M. Hwang, Program Manager, Air Force Office of Scientific Research

Leah Benard-Boggs, Program Manager, Rice University

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F. Keith Perkins (Naval Research Laboratory)

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1. Executive Summary

1.1. Preface

It is now widely recognized that graphene, the thinnest material physically in existence, has shown exceptional electronic, thermal, mechanical and optical properties. Graphene is a covalently bonded single atomic layer sheet of carbon atoms, and the fact that it could be isolated from parent graphite, a quintessential 2D layered solid, was surprising and unprecedented. The advent of graphene and the exploration of novel properties in this unique material has fascinated the scientific community worldwide. It is well known that graphene and its compounds exhibit remarkable properties which have enabled the demonstration of novel devices for a wide variety of applications in an extremely short period of time. The exploration of graphene as a model 2D system has had its impact in a variety of areas spanning physics, chemistry and engineering. Pristine 2D graphene, as well as a variety of other morphologies (e.g. ribbons) have provided fascinating insights into how this material can be modified and fabricated into novel devices for transistors, sensing, and photonics applications, to name a few.

Owing to the great success of graphene research, the question of whether 2D atomic layers from other materials can be isolated and exploited for fundamental study and applications has become very relevant. There are already reports suggesting that materials such as hexagonal boron nitride (h-BN), di-chalcogenides, tertiary compounds of carbo-nitrides, and complex oxides such as clays and zeolites can be exfoliated and isolated as stable single atomic layers. As with graphene, there are also demonstrations that some of these materials can be grown by chemical vapor deposition methods, allowing the creation of scalable large area structures, which could be further developed into devices. A good example has been hexagonal boron nitride (h-BN). Compared to graphene, h-BN is an electrical insulator and hence represents the opposite end of the spectrum as far as electrical properties are concerned. Recently there have been attempts to fabricate graphene devices on h-BN insulating substrates and these have so far given the best performance for graphene devices. Similarly, there is a whole range of compositions between boron-carbon-nitrogen and several unexplored 2D material compositions in their phase diagram. There are also other complex multi-component systems that exist as layered phases such as mica, talc which are made of alumina-silicate layers of varied compositions.

There have been already attempts to synthesize atomic layers from some of these non-graphene layered structures via chemical as well as high temperature vapor phase deposition methods. Reports exist that show non-graphene 2D atomic layers integrated into devices which exhibit exceptional performance; for example transistors derived from 2D monolayers of MoS_2 show ON/OFF ratios many orders of magnitude larger than the best graphene transistors at room temperature, with comparable mobilities. Most importantly, a variety of studies on the synthesis, chemical modification methods, device fabrication and testing and theoretical exploration of structure-property correlations have since been proposed on these stable 2D materials and the field is about to see a significant explosion of activities in the near future. It is therefore extremely timely to have such a workshop focusing on non-graphene 2D atomic layers and devices that can have an impact on technologically significant applications in the future.

1.2. Global perspective and competition in the field

The workshop had international participants who reported on the impressive progress that has been made in the 2D beyond graphene area, particularly in Europe. Notable activity in this beyond graphene area has been reported at the Trinity College (Ireland), University of Manchester (England, in graphene Nobel Laureate's group), EPFL (Switzerland), and Osaka University (Japan). Given the rate of progress overseas and the government investments made in projects such as the European Flagship Mission ($100 Million Euros per year for 10 years), the 2D beyond graphene area is poised for tremendous growth overseas. In Asia, industrial labs such as Samsung in Korea, are also at the forefront in graphene research and their focus will likely turn to other 2D material systems soon. Thus, it is imperative that similar efforts be pursued in the US in a timely manner to maintain global competitiveness in research and development in this rich and promising area. Increasing awareness with regard to international activity in this 2D beyond graphene area was another aim of this workshop.

Most of the work and publications initiated worldwide in this field have concentrated on a few materials such as hexagonal boron nitride, the dichalcogenide family and the newly discovered topological insulators. The applications that are being pursued include electronics, energy storage (electrode development using materials such as dichalcogenides), photovoltaic devices and mechanical reinforcements, where both experimental and theoretical efforts are being pursued globally.

1.3. Workshop highlights and list of topics discussed

Although the idea of separating individual layers from 2D layered solids is straightforward, the challenges in obtaining large single crystal domains, chemical modification, characterization and modeling of such materials, transfer of these layers onto appropriate substrates, manipulating these and fabricating devices are significant. The organizers and discussion leaders of the workshop have strived to provide an important forum for the workshop speakers and participants to address many of these issues and highlighting the impact this field can have in the years to come. The successful workshop that saw the participation of more than a hundred scientists from academia and national labs as well as representatives from funding agencies, discussed the emerging field of 2D layered materials beyond graphene and elaborated on the challenges and opportunities that exist in the field. This report is a summary of what transpired at the workshop and presented are the results of break-out discussions on specific target opportunities and the cross-cutting recommendations as a result of this workshop.

The list of topic addressed at the workshop involved synthesis, chemistry, device fabrication, theory and interdisciplinary approaches to tackle the key issues in the development of 2D layers of non-graphene compositions. Shown below is a list of topics that were covered at the workshop.

Layered material systems: Several material categories were discussed at the workshop; some of the prominent ones were nitrides (e.g. h-BN), oxides (e.g. vanadium and molybdenum oxides), sulfides (e.g. transition metal di-chalcogenides), carbo-nitrides (e.g. BCN, tertiary metal carbo nitrides), complex oxides (e.g. clays), other traditionally non-layered structures such as germananes (atomic layers containing germanium), silicenes (silicon based layered structures), topological insulators such as BiTe which also exhibit promise as thermo-electric materials.

Synthesis: Synthesis of high quality materials in scalable ways marks the most important challenge in the emergence of any new field. Carbon nanotubes and graphene are excellent examples of materials where roadblocks remain due to materials synthesis issues. Several talks at the workshop were dedicated to developing methods such as physico-chemical methods such as mechanical or liquid-phase exfoliation and large area vapor phase synthesis (CVD). Quality of samples and the role of defects such as grain boundaries were also discussed as being extremely relevant to the success of the field.

Materials Design: Processing of atomic layers and preparation of morphologies (e.g. nanoribbons, quantum dots), chemical modification, doping, patterning etc. have been the landmark of research in graphene and related structures due to the necessity of modifying electronic structure and hence device characteristics. These issues are also of prime importance in the case of 2D layers and were key topics of discussion at the workshop.

Characterization: Development of characterization tools and new protocols and understanding of structure at various scales has been an important piece in new materials development. The understanding of Raman spectra of nanotubes and graphene has proved to be a very valuable technique. This is going to be equally important in other 2D material systems although these techniques have not been properly developed and understood in the characterization of these new materials. Atomic level real space imaging as well spectroscopy techniques and global spectroscopy methods like Raman were discussed repeatedly with the hope that these techniques will play an important role in the 2D beyond graphene field.

Devices: New device architectures and device fabrication, as well as device characterization are going to be extremely important in the development of 2D layers for the next generation of electronic, photonic and magnetic devices. Methods to fabricate devices, device measurements, understanding electrical and optical properties that can enable novel devices were discussed in the context of applications of these 2D atomic layers beyond graphene. The extensive work on graphene devices can be a useful platform which can help guide advances in this area.

Theory: Theory and predictive modeling becomes vital in any new field to understand materials and device properties, as well as predicting new structures and materials systems. Theory of non-graphene 2D materials, theoretical studies of structure-property correlations in atomic layers and new efforts in combining tools in addressing challenges in the field were discussed. The role of theory in addressing combinatorial approaches to 2D materials design, along the lines of the national materials genome project was discussed in the break-out sessions at the workshop.

1.4. Basic challenges to be addressed in 2D layered materials and devices beyond graphene

Some of the basic broader challenges or questions to be addressed in this field are listed below:

* Synthesis of large area, large domain, defect-free crystals of 2D atomic layers
* Control of the number of layers of crystals grown on substrates
* Understanding growth mechanisms and control of growth on multiple substrates
* Development of transfer-free methods for 2D atomic layers (unlike in graphene)
* Development of solution-based bulk exfoliation methods for atomic layers
* Developing characterization methods for specimens using non-invasive techniques
* Chemical doping, modification and lattice manipulation of atomic layers to tailor electronic, optical and magnetic properties
* Development of nanofabrication approaches for atomic layer devices
* Understanding the role of contacts and interface properties in devices
* Exploration of new physics and device characteristics in atomic layer devices

* Atomic layer engineering and fabrication of hybrid devices
* Exploring new device physics arising from layer stacking of dissimilar 2D material systems that can lead to new functionalities
* Exploring interface effects which can enable new properties and new devices
* Discovery and development of new atomic layered materials for applications
* Development of modeling tools for the exploration of atomic layers and their devices
* Use of theory/modeling to probe structure-property correlation in 2D layered structures

1.5. General workshop highlights

The workshop discussed important aspects of a variety of 2D material systems and devices that could be complimentary to graphene-based systems. This new and emerging technical area and the ensuing interdisciplinary activities will be in perfect synergy with the already well-established graphene science and will impact different fields of materials science, chemistry, physics and engineering in the next decade.

In addition to the scientific community, there were several representatives from the funding agencies (NSF, DoD, DOE, NIST etc.). The workshop was co-sponsored by NSF and the AFOSR and senior management from these agencies participated and gave opening remarks as well as closing statements. As part of the workshop, NSF featured two lunch time talks focusing on their flagship programs (CREATIV and SAVI) highlighting the importance of innovation and interdisciplinary research. These talks were in synergy with the workshop goals, which essentially called for new approaches, innovations and interdisciplinary and inter-agency efforts to promote the field of 2D layered materials.

To set the stage for the meeting, the keynote presentation was given by Professor Mildred Dresselhaus of MIT, who highlighted the state-of-the-art in graphene research and the new perspectives that can emerge from exploring 2D materials beyond graphene. The enormous investment that has gone into graphene research by countries worldwide has created the excitement of a new field, as well as the challenges that are intrinsic to any new technology. She elaborated on the importance to learn the lessons from graphene research and streamline goals for successfully addressing the scientific and technological challenges in 2D layered materials. As fate would have it, Professor Dresselhaus was awarded the 2012 Kavli Prize in Nanosciences for her pioneering contributions to the study of phonons, electron-phonon interactions, and thermal transport in nanostructures, and the announcement came right after her keynote presentation at the workshop. This rightfully called for a celebration, and dignitaries including NSF Director Dr. Subra Suresh, and AFOSR Director Dr. Patrick Carrick came to honor Millie on the occasion.

Another highlight of the workshop was three breakout sessions organized to address the issues at hand in this emerging field and recommendations from the scientific community in taking this field forward. The three sessions were divided into areas related to the relevance of 2D layered materials for electronics applications, structural and energy applications, and photonic and sensing applications. Specific comments and recommendations from these sessions will be discussed later in the report.

2. List of Invited Speakers & Participants

Academic Participants and Speakers

- Pulickel Ajayan, Rice University
- Deji Akinwande, University of Texas at Austin
- Yoichi Ando, Osaka University (Speaker)
- Luis Balicas, Florida State University
- Prabhakar Bandaru, University of California - San Diego
- Sanjay Banerjee, University of Texas at Austin (Speaker)
- Kaustav Banerjee, University of California - Santa Barbara
- Seth Bank, University of Texas at Austin
- Jiming Bao, University of Houston
- Louis Bouchard, University of California - Los Angeles
- Linyou Cao, North Carolina State University
- Manish Chhowalla, Rutgers (Speaker)
- Walter de Heer, Georgia Institute of Technology (Speaker)
- Mildred Dresselhaus, MIT (Keynote Speaker)
- Randall Feenstra, Carnegie Mellon University
- Philip Feng, Case Western Reserve University
- Michael Fuhrer, University of Maryland (Speaker)
- Yury Gogotsi, Drexel University (Speaker)
- Joshua Goldberger, Ohio State (Speaker)
- Ali Javey, University of California - Berkeley (Speaker)
- Debdeep Jena, University of Notre Dame (Speaker)
- Hengxing Ji, University of Texas at Austin (Speaker)
- Swastik Kar, Northeastern University
- Philip Kim, Columbia University (Speaker)
- Andras Kis, EPFL (Speaker)
- Jeanie Lau, University of California - Riverside (Speaker)
- Lok C. Lew Yan Voon, Wright State University
- Teng Li, University of Maryland
- Xiuling Li, University of Illinois at Urbana - Champaign
- Mustafa Lotya, Trinity College Dublin (Speaker)
- Jun Lou, Rice University (Speaker)
- Zhenqiang (Jack) Ma, University of Wisconsin - Madison
- Thomas Mallouk, Pennsylvania State University (Speaker)
- Nadya Mason, University of Illinois at Urbana - Champaign
- James Murday, University of Southern California
- Saroj Nayak, Rensselaer Polytechnic Institute (Speaker)
- Ivan Oleynik, University of South Florida
- Haibing Peng, University of Houston
- Xiao-Liang Qi, Stanford University (Speaker)

- Sayeef Salahuddin, University of California - Berkeley
- Gotthard Seifert, Technische Universitat Dresden (Speaker)
- Jie Shan, Case Western Reserve University
- Vivek Shenoy, Brown University (Speaker)
- Michael Spencer, Cornell University
- Mauricio Terrones, Pennsylvania State University and Shinshu University (Speaker)
- Kang Wang, University of California - Los Angeles
- Zhenhai Xia, University of North Texas
- Huili (Grace) Xing, University of Notre Dame
- Boris Yakobson, Rice University (Speaker)
- Peide (Peter) Ye, Purdue University (Speaker)
- Alex Zettl, University of California – Berkeley (Speaker)

National Laboratory and Other Attendees

- Paul Campbell, NRL
- Cory Cress, NRL
- Adam Friedman, NRL
- David Geohegan, ORNL
- Daniel Gunlycke, NRL
- Gregg Jessen, AFRL
- Berend (Berry) Jonker, NRL
- Arnold Kiefer, AFRL
- Keith Perkins, NRL
- Jeremy Robinson, NRL
- Michael Segal, Nature Nanotechnology
- Michael Snure, AFRL
- Aniradha Sumant, Argonne National Laboratory
- Virginia Wheeler, NRL
- Colin Wood, NRL
- Yuegang Zhang, Lawrence Berkeley National Laboratory

Federal Agency Attendees

- Chagaan Baatar, ONR
- Patrick Carrick, AFOSR
- Dominique Dagenais, NSF
- Nibir Dhar, DARPA
- Bonnie Gersten, DOE
- Lawrence Goldberg, NSF
- Daniel Green, ONR
- Grace Hsuan, NSF

- Thomas Hussey, AFOSR
- James Hwang, AFOSR
- Anupama Kaul, NSF
- Susan Kemnitzer, NSF
- Bruce Kramer, NSF
- Kesh Narayanan, NSF
- Thomas Peterson, NSF
- Ian Robertson, NSF
- Pani (Chakrapani) Varanasi, ARO
- Usha Varshney, NSF
- Harold Weinstock, AFOSR
- Charles Ying, NSF
- John Zavada, NSF
- Jane Zhu, DOE

3. Program and Highlights

PROGRAM	
Wednesday, May 30, 2012	
7:15 to 8:00	**Registration and Breakfast Buffet**
8:00 to 8:20	**Welcome and Introductions** Assistant Director for Engineering: Thomas Peterson, NSF ECCS Senior Engineering Advisor: Lawrence Goldberg, NSF Division Director for DMR: Ian Robertson, NSF Chief Scientist: Thomas W. Hussey, AFOSR ECCS Program Director: Anupama Kaul, NSF
8:20 to 8:40	**Overview** Workshop Chair: Pulickel Ajayan, Rice University
8:40 to 8:50	**Funding Agency Perspectives** ENG/ECCS/NSF: Anupama Kaul, NSF MPS/DMR/NSF: Charles Ying, NSF AFOSR: James Hwang, AFOSR
8:50 to 9:30	**Keynote Presentation - Mildred Dresselhaus --- Graphene and Beyond – A Perspective**
9:30 to 9:40	**Coffee Break**
9:40 to 11:40	**Session I: Latest in Graphene and Device Applications** **Chair: Anupama Kaul, NSF**
9:40 to 10:00	**Philip Kim – Columbia** Graphene and Hexa Boron Nitride Heterostacks and Beyond
10:00 to 10:20	**Walter de Heer – Georgia Tech** Beyond 2D Graphene
10:20 to 10:40	**Michael Fuhrer – University of Maryland** Ultrabroadband Photodetection with Graphene Devices
10:40 to 11:00	**Hengxing Ji – University of Texas - Austin** Graphene-based and Graphene-derived Materials and their Properties
11:00 to 11:20	**Vivek Shenoy – Brown University** Influence of Grain Boundaries on the Physical Properties of Polycrystalline Graphene
11:20 to 11:40	**Saroj Nayak – Rensselaer Polytechnic Institute** Giant Band Gap Modulation in 2-Dimentional Structures through Dielectric Screening
11:40 am to 12:40 pm	**Working Lunch - "NSF CREATIV"** **Thomas Russell – NSF OD/OIA**
12:40 to 2:20	**Session II: Synthesis, Chemistry, Characterization and Modeling of 2D Atomic Layers** **Chair: Pani (Chakrapani) Varanasi, ARO**
12:40 to 1:00	**Yury Gogotsi – Drexel University** Two-Dimensional Carbides and Related Compounds
1:00 to 1:20	**Mauricio Terrones – Penn State and Shinshu University** Single Layer Dichalcogenides: Theory, Preparation and Characterization

1:20 to 1:40	**Thomas Mallouk – Penn State** **Synthesis of Functional Nanostructures through Topochemical Reactions of Layered Solids**
1:40 to 2:00	**Manish Chhowalla – Rutgers University** Chemically Exfoliated Layered Transition Metal Chalcogenide Nanosheets for Energy Applications
2:00 to 2:20	**Jun Lou – Rice University** Large Area Vapor Phase Growth and 2D Engineering of Atomic Layers
2:20 to 2:35	**Coffee Break**
2:35 to 4:35	**Session III: Devices and Applications of 2D Layered Materials** **Chair: James Hwang, AFOSR**
2:35 to 2:55	**Andras Kis - Lausanne** Single Layer MoS_2: Devices, Electronics and Mechanics
2:55 to 3:15	**Gotthard Seifert - Dresden** Perspectives and Limits of Transition Metal Chalcogenide Nanostructure (TMCN) Based Electronic Devices
3:15 to 3:35	**Boris Yakobson – Rice University** Probing the BCN-triangle by Computations—Outside the Carbon Corner
3:35 to 3:55	**Mustafa Lotya – Trinity College Dublin** Liquid Phase Exfoliation of Graphene and Inorganic Layered Compounds – a Route to Diverse Application
3:55 to 4:15	**Jeanie Lau – UC Riverside** 1, 2, 3: Strains, Band Gap and Many-body Physics in Graphene
4:15 to 4:35	**Debdeep Jena, University of Notre Dame** 2D Crystals: Solutions for Next Generation Electronic
4:35 to 4:45	**Coffee Break**
4:45 to 6:00	**Breakout Sessions I**
	2D Layered Materials (beyond grapheme) for Electronic Applications Chairs: Kaustav Banerjee, UCSB; Michael Fuhrer, UMD; Ivan Oleynik, USF
	2D Layered Materials (beyond graphene) for Structural and Energy Applications Chairs: David Geohegan, ORNL; Thomas Mallouk, PSU; Mauricio Terrones, PSU and Shinshu University
	2D Layered Materials (beyond graphene) for Photonic and Sensing Applications Chairs: Manish Chhowalla, Rutgers; Keith Perkins, NRL

Thursday, May 31, 2012	
7:15 to 8:00	**Registration and Breakfast Buffet**
8:00 to 10:20	**Session IV: Synthesis, Chemistry, Characterization and Modeling of 2D Atomic Layers** **Chair: Charles Ying, NSF**
8:00 to 8:20	**Alex Zettl – UC Berkeley** Synthesis, Characterization, and Opportunities for 2D Materials Based on BN and MX2

8:20 to 8:40	**Yoichi Ando – Osaka University** Progress in Topological Insulator Materials for 2D Devices
8:40 to 9:00	**Xiao-Liang Qi – Stanford University** Topological Insulator Surface States Coupled with Magnetic Materials
9:00 to 9:20	**Sanjay Banerjee – UT Austin** Novel Transistor Concepts Based on 2D systems- Graphene and Topological Insulators
9:20 to 9:40	**Ali Javey – UC Berkeley** 2D III-V XOI: Materials and Devices
9:40 to 10:00	**Peide Ye - Purdue** Device Aspects of 2D Crystals: High-k Integration, Contacts, and Scaling
10:00 to 10:20	**Joshua Goldberger - Ohio State** Germananes and Silicanes: Ge and Si Graphene Analogues
10:20 to 10:35	**Coffee Break**
10:35 to 12:30	**Breakout Sessions II**
	2D Layered Materials (beyond grapheme) for Electronic Applications Chairs: Kaustav Banerjee, UCSB; Michael Fuhrer, UMD; Ivan Oleynik, USF
	2D Layered Materials (beyond graphene) for Structural and Energy Applications Chairs: David Geohegan, ORNL; Thomas Mallouk, PSU; Mauricio Terrones, PSU and Shinshu University
	2D Layered Materials (beyond graphene) for Photonic and Sensing Applications Chairs: Manish Chhowalla, Rutgers; Keith Perkins, NRL
12:30 to 1:30	**Working Lunch**
1:30 to 2:30	**Presentations from Breakout Sessions**
2:30 to 3:15	**General Concluding Discussions (Panel Session)**
3:15 to 3:45	**Closing Remarks**
	Director of the Physics and Electronics Directorate – Patrick Carrick, AFOSR
	Deputy Assistant Director for Engineering – Kesh Narayanan, NSF
3:45 pm	**Adjournment** **Anupama Kaul and Pulickel Ajayan**
3:45 pm – Onward	**Mixer with Program Managers**

Workshop Highlights and Presenters

3.1. Session Summaries

Session I - Latest in Graphene and Device Applications: This session was dedicated to the progress and state-of-the-art in the field of graphene. Well known scientists in the graphene field presented their work and showed the progress that has been made in graphene over the last decade. In her keynote opening presentation Professor Mildred Dresselhaus from MIT described the key elements that made graphene exciting (high electron mobility and high thermal conductivity, unique dispersion relation and exceptional mechanical properties) and the progress her group has made in the use of Raman spectroscopy for characterizing and identifying graphene layers with a controlled number of layers. The importance of preparing mono- bi- and few-layer graphenes with control was highlighted. Thinking beyond graphene, she highlighted several new materials which could form the basis of work in 2D layered structures with interesting electronic properties and device possibilities. Boron nitride, sulfides and oxides, and topological insulators, and silicene were introduced. Preliminary work in fabricating field-effect transistors with high ON/OFF ratio's and good mobility in some of these materials was pointed out. In particular, the importance of basic science and discovery was highlighted and the need for looking at entirely new 2D materials, with exciting electronic structure as evidenced in structures such as $Bi_{1-x}Sb_x$ with multiple Dirac cones, was highlighted.

Several other leading scientists in graphene including Philip Kim (Columbia), Walt de Heer (Georgia Tech) and Michael Fuhrer (Maryland) talked about new results in graphene with new device demonstrations and the possibility of hybrid stacks of graphene and other 2D structures like boron nitride (Fig. 1) for exploring new space in the field of graphene as well as expanding the graphene know-how to other similar structures obtained from 2D layered materials. All the speakers emphasized the need for high quality, defect free materials and for developing processes that enable easy integration of such thin atomic layers into device architectures. The session served as an excellent precursor to the main topic of the meeting focused on 2D layers beyond graphene.

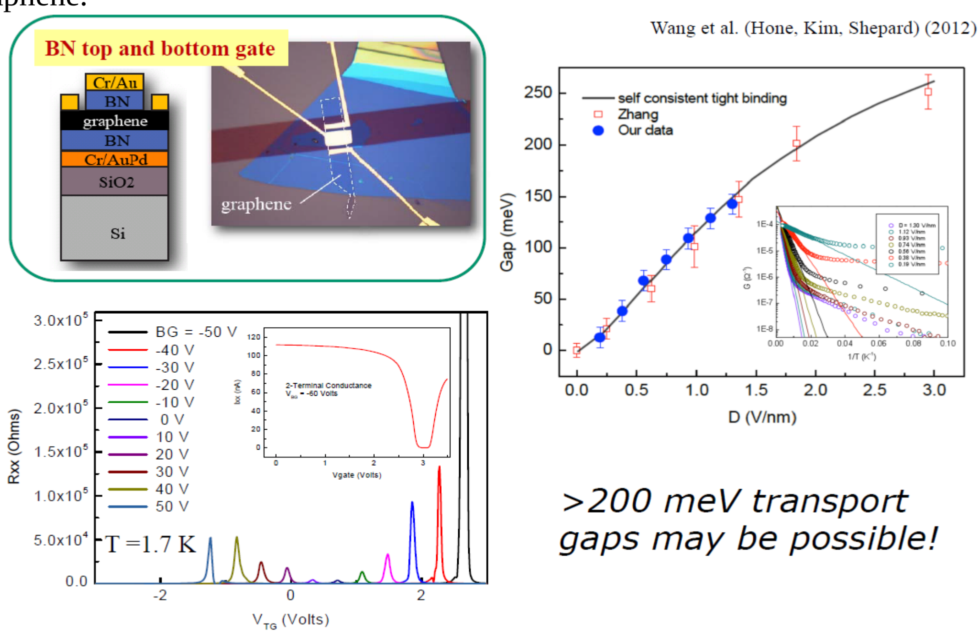

Fig. 1 Gap opening in bi-layer graphene/h-BN (Wang et al., 2012); Courtesy: P. Kim (Columbia)

Session II - Synthesis, Chemistry, Characterization and Modeling of 2D Atomic Layers: This session focused on synthesis, chemistry and characterization of various 2D layered materials beyond graphene including 2D carbides and related compounds, transition metal chalcogenides and hexagonal boron nitride (h-BN). Yury Gogotsi (Drexel) opened the session by discussing the importance of discovery and development of new atomic layered materials for various applications. By selective etching of "A" layer from "MAX" phases (here M stands for transition metals, A stands for group A elements and X stands for C and/or N) results in the formation of 2D transition metal carbides and/or nitrides called "MXenes" (Fig. 2) with tunable band gap and excellent electrical, mechanical and surface properties, rendering their potential in applications like energy storage devices, composites and flexible electronics.

Other important topics discussed in this session included synthesis of large area, large domain, defect-free crystals of transition metal di-chalcogenides and understanding of growth mechanisms and control of such 2D atomic layers growth on multiple substrates by Mauricio Terrones (Penn State) and Jun Lou (Rice). They have also discussed about the importance of developing global characterization techniques, and atomic layer engineering and fabrication of hybrid devices, respectively. Thomas Mallouk (Penn State) discussed the role of topochemical reactions in layered solids to synthesize functional 2D materials and demonstrated that H_2SO_4 and H_3PO_4 could form new intercalation compounds with h-BN. Finally, Manish Chhowalla (Rutgers) emphasized on the importance of chemistry in fabricating atomic layers with tailored electronic and other properties for energy applications.

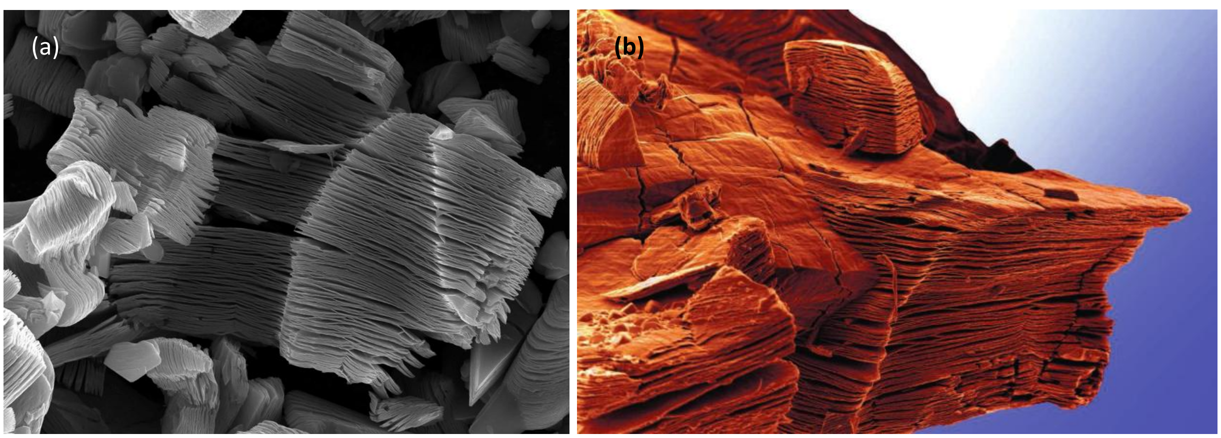

Fig. 2. (a) SEM image of Ti_3AlC_2 etched in HF 50% for 2 hours at room temperature (M. Naguib, et al. *Advanced Materials* 23, 4248 (2011)); (b) A false colored SEM image of Ti_3AlC_2 winning the People's choice award for International Science & Engineering Visualization Challenge (*Science* 335, 526 (2012)); Image Courtesy: Y. Gogotsi (Drexel).

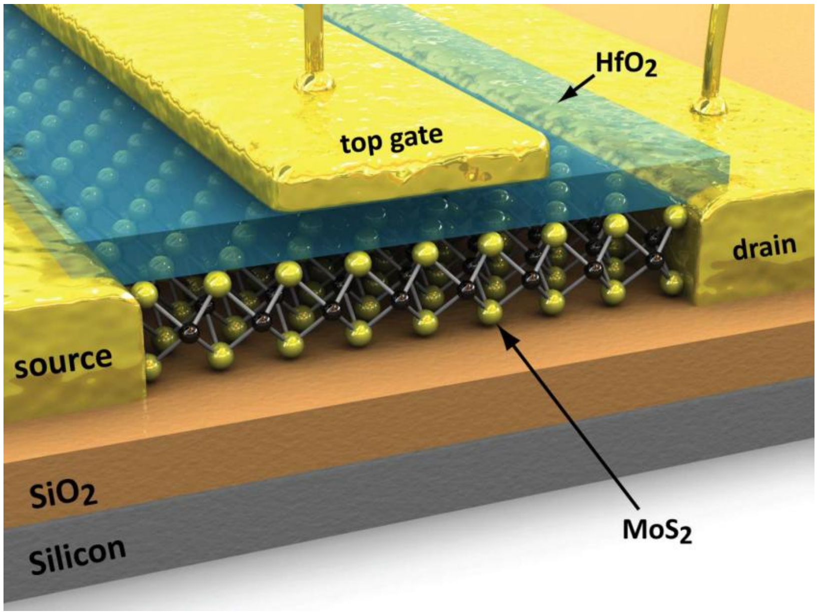

Fig. 3. Schematic illustration of a single layer MoS2 transistor (Radisavljevic et al., *Nature Nanotechnology* 6, 147 (2011)); Image Courtesy: A. Kis (EPFL).

Session III - Devices and Applications of 2D Layered Materials: In this session, while discussions on development of bulk exfoliation methods for atomic layers were continued by Mustafa Lotya (Trinity College Dublin) from last session about scale-up production of a wide variety of 2D layered materials, focus was shifted more towards devices fabrication and characterization, and modeling of 2D layered materials beyond graphene.

Andras Kis (EPFL) demonstrated single layer MoS_2 – based transistors with ohmic contacts that have high ON/OFF ratios, high mobility and low leakage currents (Fig. 3), basic electronic circuit using the same materials was also successfully made. In Jeanie Lau's (UC Riverside) talk new physics and device characteristics in atomic layer devices was discussed while Debdeep Jena (Notre Dame) discussed new nanofabrication approaches for realizing atomic layer devices. Another important aspect of this session was the role of theory/modeling to probe structure-property correlation in 2D layered materials, as presented by Boris Yakobson (Rice). In addition, Gotthard Seifert (Dresden) discussed the development of modeling tools for the exploration of 2D atomic layers and devices.

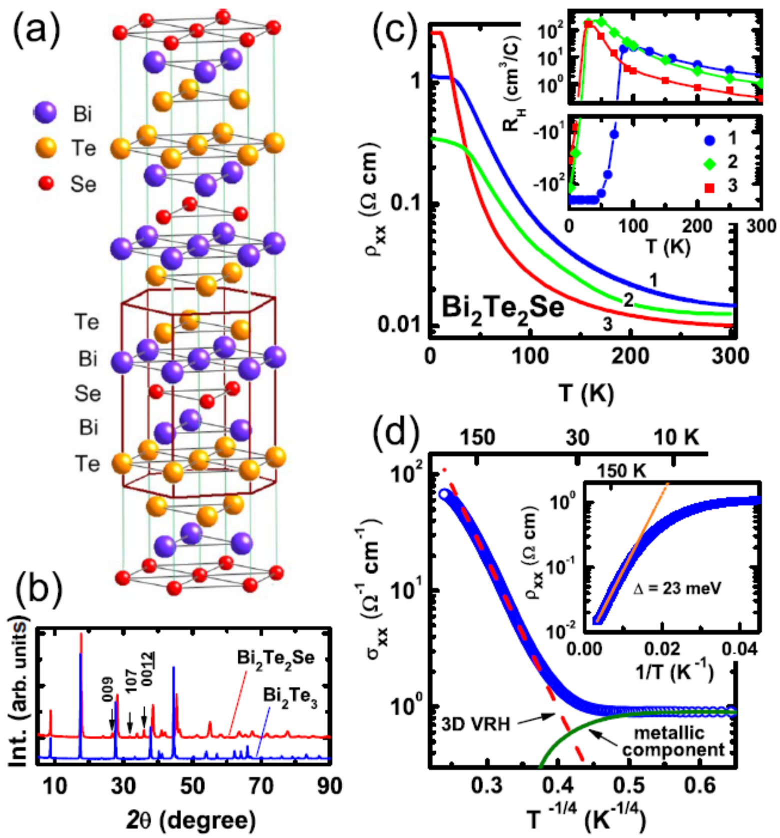

Fig. 4. (a) Layered crystal structure of Bi_2Te_2Se showing the ordering of Te and Se atoms. (b) Comparison of the x-ray powder-diffraction patterns of Bi_2Te_2Se and Bi_2Te_3. Arrows indicate the peaks characteristic of Bi_2Te_2Se. (c) Temperature dependence of resistivity for samples 1–3. (d) Plot of the conductivity vs. temperature for sample 1. (Ren, Ando et al., *Phys. Rev. B* (2010)); Courtesy: Y. Ando (Osaka).

Session IV - Synthesis, Chemistry, Characterization and Modeling of 2D Atomic Layers: This session included several fascinating talks on materials that can be considered as quasi-2D. These include materials such as topological insulators where the bulk material remains insulating but retains a metallic surface state. Topological insulators present several physics challenges as well as opportunities in device physics. Several groups world-wide are working on materials and device aspects of topological insulators and have focused on materials such as Bi_2Te_3, Bi_2Se_3 as well as ternary compounds such as Bi_2Te_2Se (Fig. 4). Other 2D materials include III-V semiconductor compounds (e.g. InAs) and recently there have been efforts to make ultra-thin films of these materials. Such quasi-2D materials also provide alternative routes to achieving atomically thin device architectures which could be integrated with true 2D layered materials. Finally, traditionally 3D materials such as silicon and germanium can have 2D analogues and new chemistry approaches to make silicon and germanium containing (silicenes and germananes) 2D layers were described in this session. Once again, the common theme was on the development of good-quality materials, innovative techniques for materials processing as well as device fabrication. As the field evolves there will be synergy between these quasi-2D materials and other traditionally layered materials. There was also a strong element of theory in the understanding of complex materials such as topological insulators.

4. Break-out Session Recommendations

Three break-out sessions focusing on different aspects of technological applications of 2D materials beyond graphene had drawn very enthusiastic participations from all workshop attendees. The discussions were centered on the following questions:

1) Current state of the field (materials, devices, modeling) and the application areas in which these materials systems are likely to have the biggest societal impact (energy, photonics, electronics, sensing…etc)?
2) What is needed in the national science infrastructure to transform the promise of this field to an area of US scientific and technological strength?
3) What are the key areas in which knowledge and resources limit the progress of this field which may prevent us from reaching the desired goals?
4) What lessons can we learn from carbon nanotubes that will help speed up R&D of 2D materials and devices?
5) How are other countries positioned to carry out research in this area and how did they get there?

The summary of the group recommendations generated from such discussions from each break-out session is provided below.

2D Layered Materials (beyond graphene) for Electronic Application

Need to understand metrics for good performance beyond state of the art: example is that mobility is not useful at 22nm. What are the figures of merit for new devices being considered?

- Need to understand the applications where 2D materials could play a role – what is the device we want to make? Flexible electronics, optoelectronics? Performance should be driver. But need to find the applications where performance will be far superior.
- Need to address challenges where state of the art is not advanced:
  - Scaling up to large-area uniform materials
  - Contacts
  - Atomic-scale control (lateral and vertical) and edge state control
  - Stacking of 2D multilayers in controlled ways
  - Establishing dielectrics on 2D materials
  - Gate control
  - Doping and impurity/defect control (Need "MBE-quality" materials!)
  - Development of new simulation capabilities specifically tailored for 2D materials and devices, must be coupled to experiments, interdisciplinary teams encouraged
  - In-situ characterization capabilities
- Need to understand where US industry will compete and performance is the key. US does not currently have best materials capability in growth/production of 2D materials, including their precursors. Urgent need for fab quality 2D materials for device development. Example: DARPA GaN program – supplies university researchers with highest quality GaN for research – similar programs for 2D materials? Can funding agencies incentivize this?

- Need to have standardized, well-characterized precursor materials (graphite, MoS2, hBN) and program to share materials. (An experimental "materials genome project"?)
- Need funding to transfer device prototypes to a technology. Need closer connection to industry/end user of technology so the requirements of technology are known.
- Metrics for benchmarking devices are needed. Is there a roadmap for technologies outside ITRS/CMOS? How do we know what is needed that doesn't yet exist? Need a "wish list" for new technologies. Industry input is critically needed.
- Need to find out whether there are fundamental scientific issues remaining to be addressed. Game-changing technologies probably need qualitatively new science: quantum computing, Majorana fermions, exciton condensates, etc.
- Funding agencies should support fundamental discovery-based research with no particular application in mind. Culture of panel review does not favor high-risk proposals.
- Need to establish a fundamental materials properties database for 2D materials (similar to the materials genome project).
- Need better connections across interdisciplinary boundaries (physics/chemistry/engineering). Funding agencies should incentivize this. Especially cross-boundary education. This is a type of "outreach".
- Stability of funding in basic science as well as development of novel applications in 2D materials is needed. Funding cycle should be better synched to graduate student studies duration. "Bandwagon" boom-and-bust cycles not good for science. Need to reward steady progress, not just jumping to the latest thing.
- Need for mechanism to fund equipment purchase/development for the individual PIs. (MRI inadequate as it rarely longer funds state-of-the-art individual-PI equipment). Opportunity for NSF to collaborate with DURIP?
- New tools for fundamental characterization of 2D materials, interfaces, junctions etc.
- EU will fund graphene research at EUR$1B over ten years (Flagship). Korea has major industrial funding of 2D materials. US companies appear to be involved only at level at which they can obtain government funding. Need to identify the mechanisms by which US R&D funding benefits US industry: Training of skilled workforce? Development of IP in US?

2D Layered Materials (beyond graphene) for Structural and Energy Applications

- Still in discovery and design phase – many new materials call for exploration of characterization and processing techniques, and functionality
- Possible structural and energy applications include both on-substrate and free-standing configurations:
    - Electrodes - Flexible transparent conductive electrodes for macroelectronics and for organic electronics (PV, LED)
    - Catalysts – for hydrogen evolution, for industry, photocatalysts
      - replacing noble metals
    - Coatings
    - Thermal materials – Thermal management, thermofluids, adding thermal conductivity to polymer composites
    - Composite Materials – Electrically and thermally conductive, high strength, high toughness

- Energy storage / generation media - Batteries, supercapacitors, fuel cells
    - Hydrogen Storage media
    - Water purification and desalination
    - Thermoelectric materials
    - Lubricants
- Need to establish stronger connections between basic science explorations, nanomanufacturing initiatives, and industry
    - Interagency cooperation
    - Science to scalable nanomanufacturing process - (e.g. NSF scalable nanomanufacturing (3-5 investigator projects, 5-6 M$))
    - Missing link: Industry-driven prototyping (researchers + industry) – ARPA-E
    - Advanced manufacturing – (e.g., inclusion into initiatives in EERE (Manufacturing Demonstration Facilities), NIST (1B$ + 1B$ match, 15 programs for NNI (Nat'l. Network for Manufacturing Innovation), pilot for additive manufacturing etc.)
- Needs for establishment of standards for material quality and performance
- Need for reproducibility of material quality after large scale production methods
- Need to address synthesis and processing challenges.
    - Still discovering the types of entirely new 2D materials we can access (e.g. new MXenes, silicene, germanene, oxides,)
    - Role and opportunity of defects very important for new composites
    - For chemical functionalization and organic hybrid materials development
    - Three dimensional constructs of 2D materials must be considered as properties are evaluated for structural/energy applications
    - Exfoliation without damage to properties
    - Obtaining preferentially single layers in stable suspensions, stable dispersions
    - Methods of alignment during processing
    - Fundamental understanding of growth mechanisms – e.g. CVD for large single crystals, rapid growth over large areas,
    - How to prepare / characterize clean interfaces
- Multi-scale characterization tools needed
- Need to address theory/modeling challenges:
    - For general purpose synthesis: "optimization with constraints"
    - Computational design of substrates promoting nucleation into 2D (layer) and preventing nucleation into 3D (bulk).
    - For electrochemical energy applications
        - Energy landscapes assessment for ionic binding and mobility on the 2D substrates and between the layers.
    - For structural/mechanical and multifunctional:
        - Theoretical mechanisms of interface control, with the challenge of sufficiently strong binding yet preserving the structural integrity of 2D-layers.
- Large scale nanomanufacturing efforts in Australia, Europe, Japan, US needs to step up the efforts in this area

2D Layered Materials (beyond graphene) for Photonic and Sensing Applications

- Need to address challenges for Sensors in General:
    - Specificity
    - Signal to noise ratio; signal to information ratio!
    - Minimization of false positives, false negatives
    - Standoff/range vs. point
    - Power
    - Affordability, performance compared to existing tools
    - Portability/lightweight if required
    - Integration
    - Radiation hardness
- Need to take advantages of 2D Materials
    - Vast chemistry provides platform for designing sensors for specific applications: Concepts that exploit the rich chemistry of 2D materials without deteriorating the transport and optical properties; Control of transport properties (energy gap, carrier density) apparently possible in materials with a wide range of surface chemistry.
    - Purely surface and charge quantization
    - Variable electronic structure provides opportunity to integrate optical detection
    - Maybe advantages compared to top down approach of making 2D from 3D materials
    - Mechanical flexibility may provide opportunities for integration onto inexpensive platforms, with caveats: anything beyond cylindrical substrates is a practical challenge
- Inexpensive chemical/solution based methods for producing optically and electrically active 2D materials for R&D should be explored. This is an enabling technology.
- 2D materials may be ideal for sensors exploiting optical (stand-off) means for detection: molecular adsorption can be successfully and efficiently interrogated optically due to magnified effects on electronic structure in a film already highly absorbent
- New measurements show that the optical absorption in 2D materials is related to the fine structure constant times the number of allowed inter-band transitions ("quantum absorbance" Javey et al.)
- Observation of photoluminescence (PL) in a number of 2D materials needs to be exploited for sensing applications, and methods to increase the quantum yield of PL in layered transition metal dichalcogenides (LTMDs) should be explored
- d-orbital conductivity in metallic layered transition metal dichalcogenides (m-LMTDs) makes them rich for exploration of optical properties
- Low band gap 2D materials for plasmonic and/or spintronics should be explored
- Doping to modulate the carrier density and exploitation of excitonic effects in layered 2D materials should be investigated

5. Cross-cutting Recommendations and Goals

The discussions at the workshop showed the emergence of a new field based on the creation and manipulation of atomic layers from a wide range of layered materials. This is pre-empted by the vast body of work based on graphene. The story of “2D layered materials beyond graphene” has similarities and differences with the story of graphene itself. The recognition that there are a large number of layered compounds, similar to graphite – the precursor to graphene, allows one to think about strategies to extract individual layers from these compounds and explore their properties. Graphene had special attributes such as the existence of massless Dirac Fermions and the high mobility of charge carriers making it a very unique electronic material. However, the complimentary compositions of structures similar to graphene allow the entire spectrum of electronic properties (metal-semiconductor-insulator) to be explored. Some of the obvious materials in the category are the nitrides and oxides (insulator), dichalcogenides (semi-conductors and unique materials such as topological insulators), boron-carbon-nitrogen containing ternary materials (range of electronic properties), complex structures such as clays, mica etc. and several others including metastable layered phases of non-layered materials. However, these new atomic layers need to be studied for their physical properties and potential for applications. Many of the talks presented at the workshop essentially captured this sense that fundamental issues needs to be addressed, lessons learned from the graphene field need to be seriously considered, and interdisciplinary approaches need to be implemented to help accelerate this new and emerging field of 2D layers beyond graphene into a fundamentally exciting and technologically relevant field for the next decade or so. Some of the cross-cutting recommendations and goals deduced from the workshop are listed below and these could serve as a blue print for investment in this area, as well as guide to funding key innovative science/technology programs in the near future.

1) **New materials genome effort in 2D layered materials:** The Materials Genome Initiative (MGI) envisioned by US President Barak Obama’s administration is essentially tuned to significantly enhancing the speed at which new materials are discovered, developed and made ready for manufacturing. This is also related to the recently announced National Nanotechnology Signature Initiative (*Nanotechnology Knowledge Infrastructure (NKI): Enabling National Leadership in Sustainable Design*). There may be many classes of materials that could be chosen for this discovery-development platform; the 2D materials have the essential features that would qualify for this inititative. Notwithstanding the enormous success of graphene, the bottleneck has been in the materials quality control, large scale manufacturing feasibility and integration into device platforms. The emergence of the 2D layered material systems could be considered in the light of MGI, both in experimental and theoretical efforts. A cross-cutting effort to develop strategies for material development with manufacturing and device integration possibilities should be considered. Long-term sustainable center-like efforts should be funded, co-sponsored by multiple agencies and industry wherever applicable, to enable scalable manufacturing of high quality 2D layered materials.

2) **Theory and predictive modeling driven effort to identify 2D layers and their hybrids:** Theory and modeling has been the force behind nanotechnology and for materials such as carbon nanotubes and graphene. Theoretical efforts have been extremely useful in predicting material behavior. For the 2D layered materials effort, we recommend a concerted effort to identify new 2D atomic layers with specific properties that would enable device development, new hybrid material systems using 2D atomic layer building blocks and new physical properties predicted for 2D layered material systems and their engineered structures. We recommend small group projects (along the same lines of NSF NIRT) focusing on different

aspects such as computational materials design of 2D atomic layers, defect engineering and structure-property correlations in 2D atomic layers, electronic and optical properties and device performance of 2D atomic layer based structures etc.

3) **Additive manufacturing efforts to synthesize scalable 2D layered materials**: This would again be in the form of centers or interdisciplinary research groups focused on solving manufacturing challenges in 2D layered materials. Development of processes and tools for large scale deposition of 2D layers and chemical protocols for bulk synthesis of atomic layers, basic research programs coupled with manufacturing focus to solve materials consistency issues, modeling and simulation to understand growth processes etc. could be part of this effort. Collaboration with industry partners, especially with large tool manufacturers and small businesses to enter the manufacturing field for the realization of 2D layered materials would be welcome. Academia-industry such as the NSF GOALI could serve as a model but funded through inter-agency resources.

4) **Development of characterization tools and methods for 2D layered materials**: Characterization tools and the development of new methods to analyze 2D atomic layers would enable accelerated development of the field since proper materials characterization was the bottleneck in many recent materials areas including that of graphene. Focused group efforts in this area (through interdisciplinary groups – material growers, theorists and characterization experts) are recommended.

5) **Development of device strategies using 2D layers**: It has been said that "those who control materials control technology". This has been true in some cases but in several of the new materials (e.g. nanotubes, graphene etc.) this has not proven to be the case. The issue has been compounded by several factors, including scalable manufacturing, performance with industry benchmarks, time-lag in getting disruptive technologies to commercial space etc. Creation of academia-industry axes in the development of applications and subsequent commercialization of technologies based on 2D layers will be important. The construction of 3D devices where 2D systems are used as building blocks can unveil new opportunities and new device functionalities for applications in electronics, photonics, plasmonics, photo-voltaics, sensing, spin-based magnetic systems and related areas. Integration of 2D dielectrics with 2D semiconducting layers and the choice of substrates will likely impact overall device performance and optimizing such devices should prove vitally important for high frequency electronics applications for example. Similar to what has happened in the graphene field, constant innovations in identifying and demonstrating new device concepts and showing its competitiveness to existing technologies (e.g. silicon based) is important and this should be promoted with new initiatives to fund single PI research in the area as well as larger programs that would be part of center-efforts or other DoD MURI like efforts. The collaboration of industry and as well as support of SBIR type efforts will also be important to establish the viability for 2D layered materials in device applications.

6) **Cross-agency and international collaboration in 2D layered materials research**: The significant impact of nanotechnology was facilitated through agency-wide initiatives and international collaborations to support basic research and individual innovations. The promotion of research in this area of 2D layered materials and devices should follow this example to create broad initiatives at all levels, from basic science to applied research.

6. Broader Impact

The scientific activity in this emerging area will impact several interdisciplinary scientific developments in the next decade and will positively impact learning in science and engineering disciplines. Graduate students and post-doctoral fellows will be impacted as they will be undertaking important research assignments in this field and the workshop has set broad directions for future research in this area.

Education and Outreach

- As emphasized repeatedly during the workshop and also in this report, breakthrough and progress in the field of 2D materials and devices beyond graphene will benefit tremendously from research that draws on many disciplines including physics, chemistry and engineering, thus it is only natural to enable scientists and engineers to work together more effectively in research teams involving synthesis, chemistry, characterization, theory and device fabrication. Research in general, and students in particular, will benefit from working in multidisciplinary teams.
- Cross-boundary educational efforts, due to the nature of the research, should be strongly encouraged in order to train talent in the US who can then contribute effectively to scientific discovery and engineering innovation in this emerging field. Reaching out to American industry partners is critical to streamlining the training of skilled future workforce and the development of 2D materials and devices beyond graphene presents an ideal platform for such activities due to the high degree of technical relevance to many important applications. In particular, the electronics industry (e.g. SRC, semiconductor research consortium) has championed the case of graphene research through several programs such as the Nanoelectronic Research Initiative (NRI) or the South West Academy of Nanoelectronics (SWAN) center, just to name a couple. Developments in 2D layered materials beyond graphene could be clearly interesting to this sector, and collaboration with federal agencies (NSF) and industry initiatives (NRI), can enable research leadership for the US in this emerging area. The exchange programs for students with international hosts engaged in strong programs in the 2D materials and devices area could also be a direction to consider. NSF (OISE) could consider funding supplemental grants to PIs already funded in the area to promote such educational activities.
- It is very obvious from the workshop that the community currently engaged in this exciting research area is very eager to enhance outreach efforts to the younger generation, their teachers, and the public to improve diversity and societal awareness.

7. Conclusions

The workshop on 2D layered materials and devices beyond graphene was a successful attempt to define an emerging field that has sprouted at the heels of the large body of graphene work. It was recognized by several speakers at the workshop that this was a timely topic with immense potential for future science and technology. The high level of interest shown by the large spectrum of scientists points to the acceptance of this theme as the next big thing in materials after graphene. The discussions at the workshop considered avenues and directions for the development of 2D atomic layer based structures as building blocks for the next generation of devices and nano-architectures. It is imperative that the right amount of resources be made available and invested to bring innovative ideas in order to make the field competitive and fruitful for future technologies. The basic science and engineering efforts in this area should be encouraged and supported so that discoveries ensue and lead to new technologies in the future. It was broadly acknowledged that the range of possibilities that exists in the area of 2D layered materials will surely give graphene a run for the money. In addition several other countries, especially those in Europe, have already started to invest significantly in this area. They are poised to deliver forefront research and it is imperative that the US establishes similar efforts to remain competitive globally.