Massachusetts Institute of Technology
Lincoln Laboratory

Valleytronics Materials, Architectures, and Devices Workshop

MIT Samberg Center, Cambridge, MA

22-23 August 2017

Organizing Committee:

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ABSTRACT

Both classical and quantum computing face significant challenges. On the classical side, silicon field effect transistors are reaching the fundamental limits of scaling and there is no replacement technology which has yet demonstrated even comparable performance to the current generation of commercially available silicon CMOS. On the quantum side, scaling the number of entangled superconducting or trapped ion qubits to that required to solve useful problems is an enormous challenge with current device technology. Both fields stand to benefit from transformational devices based on new physical phenomena. Two-dimensional materials such as graphene and transition metal dichalcogenides (TMDs) possess a number of intriguing electronic, photonic, and excitonic properties. This whitepaper focuses on their valleytronic properties, which are truly unique to this new class of materials. A lack of inversion symmetry coupled with the presence of time-reversal symmetry endows 2D TMDs with individually addressable valleys in momentum space at the K and K' points in the first Brillouin zone. This valley addressability opens the possibility of using the momentum state of electrons, holes, or excitons as a completely new paradigm in information processing with significant advantages over the state of the art. First, topologically protected valley currents may be dissipationless, eliminating the I^2R power consumption in conventional electrical interconnects. Second, valley filters may not be limited by the same 60 mV/decade thermodynamic minimum which inhibits reducing the operting voltage of traditional MOSFETs. Third, Boolean operations performed in momentum space may eliminate the need for MOSFETs entirely, and could reduce the energy scale for operations by more than an order of magnitude from the current 900 meV to less than 30 meV. For quantum computation, qubits constructed out of valley quantum dots may benefit from long coherence times or more relaxed temperature requirements due to valley protection of the spin states.

A workshop sponsored by the MIT Lincoln Laboratory Technology Office and the National Science Foundation gathered leading researchers to define the opportunities and challenges in developing valleytronic technologies for useful applications. This whitepaper summarizes the collective thoughts of this community.

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1. PURPOSE OF THE MEETING

The Valleytronics Materials, Architectures, and Devices Workshop, sponsored by the MIT Lincoln Laboratory Technology Office and co-sponsored by NSF, was held at the MIT Samberg Center on August 22-23, 2017. Valleytronics is an emerging field which promises transformational advances in information processing through the use of a charge carrier's momentum index in conjunction with its charge and/or spin. Isolation of 2D materials such as graphene[1-3] and transition metal dichalcogenides[4, 5] has allowed realization of experiments which confirm our understanding of valley physics. However, development of useful devices for valleytronic computing or other technologies requires significant advancements in material quality, device designs, and circuit architectures.

This event gathered the leading researchers in the field to present their latest work and to participate in honest and open discussion about the opportunities and challenges of developing applications of valleytronic technology. The workshop, originally limited to 42 attendees, “sold out” within three days of the initial announcement. This highly successful meeting included 16 invited talks by the most prominent faculty and scientists studying the solid-state physics of valleytronic two-dimensional materials. More importantly, three interactive working sessions were held which tackled difficult topics ranging from potential applications in information processing and optoelectronic devices to identifying the most important unresolved physics questions. A poster session allowed students and postdocs to present their latest findings in a relaxed and congenial atmosphere and to discuss their work with well-known faculty and scientists.

A tangible product of the workshop is this whitepaper which aims to inform the reader on potential benefits of valleytronic devices, on the state of the art in valleytronics research, and on the challenges to be overcome. We are hopeful this document will also serve to focus future government-sponsored research programs in fruitful directions.

2. LIST OF PARTICIPANTS

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We would like to acknowledge Ann Spanos from MIT Lincoln Laboratory for providing invaluable administrative support for the workshop.

3. MEETING ORGANIZATION

The meeting was structured to encourage frank discussion and thinking about higher-level topics such as the potential applications of valleytronics, as opposed to narrow technical discussions. Technical talks in the morning provided intellectual stimulation for the breakout discussions in the afternoon. Talks were not arranged into sessions by topic; instead different areas such as theory, material growth, and device measurements were roughly evenly distributed throughout the program to promote cross-connections between different disciplines.

The afternoons were spent in breakout sessions. The attendees were divided into three groups, with the intent to have both theorists and experimentalists in each group. The same groups met for both days. The first day was more free-form and allowed for brainstorming on the topics, whereas day two allowed for deeper exploration and crystallization of the emerging ideas. The breakout sessions were charged with providing actionable output on the following three topics:

Breakout Session #1: Current State of Knowledge

- Summarize what we know about Valleytronics
- What are the key physics? What is different? Why is this important?
- What are the milestone achievements in the field in the past 10 years or so?
- What are the important unresolved physics questions?

Breakout Session #2: Emerging Opportunities

- What are the information processing opportunities that can benefit from Valleytronics?
- What other applications are possible?
- What are the big challenges or questions to enable any of these technologies?

Breakout Session #3: Material and Device Needs

- Summarize what is known about Valleytronic materials and their important fundamental characteristics
- How do the materials need to improve? Defect density, domain size, characterization techniques, what else?
- What is the state of the art of devices which have been built, and what needs to come next?

4. FULL AGENDA

Tuesday August 22

7:30 AM	Registration / Breakfast
8:00 AM	Opening Remarks, *Steven Vitale, MIT Lincoln Laboratory*
8:15 AM	Valley carrier lifetime and valley current in WS_2/WSe_2 heterostructures, *Feng Wang, University of California at Berkeley*
8:45 AM	Optoelectronic properties of interlayer excitons in atomically thin van der Waals heterostructures, *Philip Kim, Harvard University*
9:15 AM	Electrical generation of valley magnetization in 2D materials, *Jie Shan, Pennsylvania State University*
9:45 AM	Open Discussion
10:00 AM	Break
10:15 AM	VOI based valleytronics in graphene, *Yu-Shu Wu, National Tsing-Hua University, Taiwan*
10:45 AM	Fabrication of VdW heterostructures and synthesis of high-purity TMDCs, *Jim Hone, Columbia University*
11:15 AM	Exploring the bright side and the dark side of excitons in atomically-thin transition metal dichalcogenides, *Alexander High, University of Chicago*
11:45 AM	Open Discussion
12:00 PM	Lunch
1:00 PM	Quantum transport and optoelectronics in van der Waals heterostructure, *Pablo Jarillo-Herrero, Massachusetts Institute of Technology*
1:30 PM	2D magnets and heterostructures, *Xiaodong Xu, University of Washington*
2:00 PM	Theory of local valley filtering, *Daniel Gunlycke, Naval Research Laboratory*
2:30 PM	Valley and spin-polarized electrons in 2D semiconductors, *Kin Fai Mak, Penn State University*
3:00 PM	Open Discussion
3:15 PM	Break
3:30 PM	Breakout Sessions
5:00 PM	Breakout Session Outbriefs
5:30 PM	Poster Session, Reception and Networking
6:30 PM	Adjourn

Wednesday August 23

7:30 AM	Registration / Breakfast

8:00 AM	Observation of valley-selective optical Stark shift and Bloch-Siegert shift in monolayer WS_2, *Nuh Gedik, Massachusetts Institute of Technology*
8:30 AM	Theory of the valley and spin Hall effects, *Allan MacDonald, University of Texas at Austin*
9:00 AM	Controlling excitons in 2D semiconductors by optical and magnetic fields, *Tony Heinz, Stanford University*
9:30 AM	Open Discussion
9:45 AM	Break
10:00 AM	Valley, pseudospin, and chirality polarisation in graphene- boron nitride heterostructures, *Artem Mishchenko, University of Manchester, UK*
10:30 AM	Strain fluctuation enhanced valley Hall effect, *Di Xiao, Carnegie Mellon University*
11:00 AM	Gate-controlled spin-valley locking of resident carriers in WSe_2 monolayers, *Scott Crooker, Los Alamos National Laboratory*
11:30 AM	Open Discussion
11:45 AM	Lunch
12:45 PM	Breakout Sessions
2:15 PM	Breakout Session Outbriefs
3:00 PM	Closing Comments
3:10 PM	Post-Workshop Organizing Committee Meeting
4:00 PM	Adjourn

5. INTRODUCTION TO VALLEYTRONICS

Periodic semiconductor crystal lattices often have multiple degenerate minima in the conduction band at certain points in momentum space. We refer to these minima as valleys, and devices which exploit the fact that electrons are present in one valley versus another are referred to as valleytronic devices. Though degenerate valleys are present in many periodic solids, in most cases it is impossible to address or manipulate carriers in one valley independently from another as the valley state of a carrier is not strongly coupled to any external force we can apply. Thus it is not practical to construct useful valleytronic devices out of most materials. This is in contrast to spintronics, for example, where the electron spin is readily manipulated by magnetic fields through the electron spin magnetic moment or (less easily) by electric fields through spin-orbit coupling.

In some materials, carrier mass anisotropy along different crystal orientations can result in valley polarization; preferential scattering occurs from one valley into another. This has been shown in diamond, aluminum arsenide, silicon, and bismuth at cryogenic temperatures. However, these materials still lack a strong coupling between the valley index (sometimes called the valley pseudospin) and any external quantity such as an applied field. It is not clear that there is a way to use mass anisotropy to produce a useful device such as a switch. So we do not consider this class of materials in our discussion of valleytronics.

The isolation of 2D materials such as graphene and monolayer MoS_2 were seminal events in the field of valleytronics. In stark contrast to all other materials, these possess valleys at the inequivalent K and K' points in the Brillouin zone (see Figure 1), which exhibit strong valley-selective interactions with applied electric and magnetic fields. [Note that some authors use K' and others use –K to represent the non-K valley; we use –K and K' interchangeably in this paper.] As one can see in the histogram of publications in the field in Figure 2, the isolation of graphene in 2004 catalyzed new research in valley physics, but the isolation of the first monolayer transition metal dichalcogenide (TMD) in 2010 caused an explosion in the number of valleytronic publications. The following discussion explains why the fundamental symmetries of these monolayer materials is critical to valley addressability; it is largely based on published work in references [6-8].

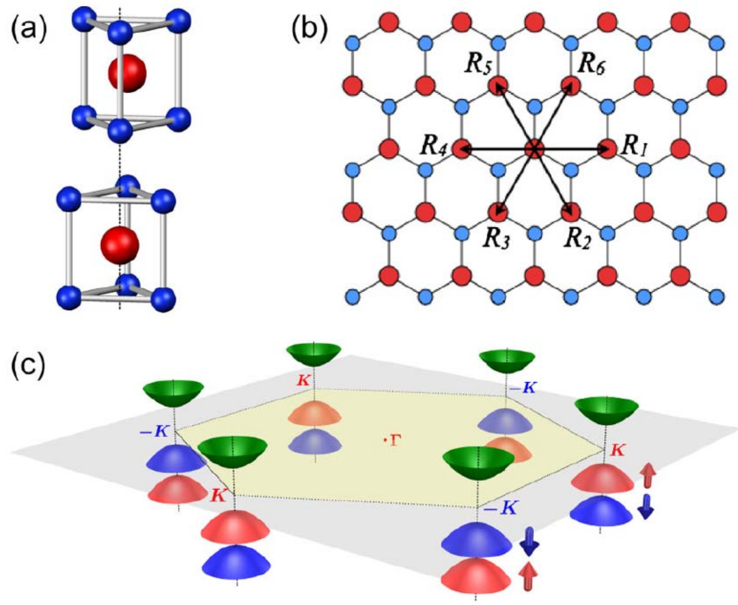

Figure 1: TMD crystal structure and Brillouin zone. From reference [8].

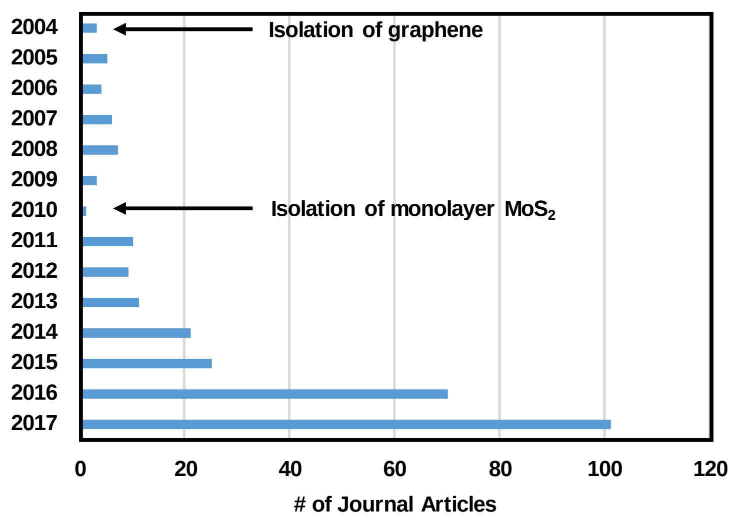

Figure 2: Number of relevant publications per year with "Valley" or "Valleytronic" in the title.

5.1 VALLEY CONTRASTING PHYSICS

The K and K' points in hexagonal 2D materials are time-reversed images of one another, so in general physical qualities that have odd parity under time reversal are good candidates to distinguish valley states. For example, if at the K and K' points the Berry curvature and orbital magnetic moment are non-equivalent one can in principle distinguish between the valleys using electric and magnetic fields, respectively. However, if inversion symmetry is present, it would render both the Berry curvature and orbital magnetic moment vanishing because they are pseudovectors. This is shown below.

The equations of motion for Bloch electrons under applied electric and magnetic fields are:

$$\dot{\boldsymbol{r}} = \frac{1}{\hbar}\frac{\partial E_n(\boldsymbol{k})}{\partial \boldsymbol{k}} - \dot{\boldsymbol{k}} \times \Omega_n(\boldsymbol{k})$$

$$\hbar\dot{\boldsymbol{k}} = -e\boldsymbol{E} - e\dot{\boldsymbol{r}} \times \boldsymbol{B}$$

where Ω is the Berry curvature defined in terms of the Bloch functions,

$$\boldsymbol{\Omega_n}(\boldsymbol{k}) = \nabla_{\boldsymbol{k}} \times A_n(\boldsymbol{k})$$

$$A_n(\boldsymbol{k}) = i\int u_n^*(\boldsymbol{r},\boldsymbol{k})\, \nabla_{\boldsymbol{k}} u_n(\boldsymbol{r},\boldsymbol{k})\, d^3\boldsymbol{r}$$

A_n is the Berry connection and u_n is the periodic part of the Bloch electron wavefunction in the n^{th} energy band. The Berry curvature can also be written as

$$\boldsymbol{\Omega}_n(\boldsymbol{k}) = i\frac{\hbar^2}{m^2}\sum_{i\neq n}\frac{\boldsymbol{P}_{n,i}(\boldsymbol{k}) \times \boldsymbol{P}_{i,n}(\boldsymbol{k})}{\left[E_n^0(\boldsymbol{k}) - E_i^0(\boldsymbol{k})\right]^2}$$

Where $E_n^0(\boldsymbol{k})$ is the energy dispersion of the n^{th} band, and $\boldsymbol{P}_{n,i}(\boldsymbol{k}) = \langle u_n|v|u_i\rangle$ is the matrix element of the velocity operator. The Berry curvature describes the geometric properties of the Bloch bands, and is central to the understanding of topological insulators and other band topology related effects. By demanding that the equation of motion must remain invariant under the system symmetry, one can see that with time-reversal symmetry, $\boldsymbol{\Omega}_n(\boldsymbol{k}) = -\boldsymbol{\Omega}_n(-\boldsymbol{k})$, and with inversion symmetry $\boldsymbol{\Omega}_n(\boldsymbol{k}) = \boldsymbol{\Omega}_n(-\boldsymbol{k})$. Thus only when inversion symmetry is broken can valley-contrasting phenomena manifest. From the equations of motion we see that if an in-plane electric field is applied in a 2D crystal then a non-zero Berry curvature results in an anomalous electron velocity perpendicular to the field, and the velocity would have opposite sign for electrons in opposite valleys.

The broken inversion symmetry also allows the existence of an orbital magnetic moment. Intuitively, it can be regarded as due to the self-rotation of an electron wavepacket. The electron energy dispersion in the n^{th} band is modified to,

$$E_n(\boldsymbol{k}) = E_n^0(\boldsymbol{k}) - \boldsymbol{m_n}(\boldsymbol{k}) \cdot \boldsymbol{B}$$

where the quantity **m** is the orbital magnetic moment, given by:

$$\boldsymbol{m}(\boldsymbol{k}) = i\frac{e\hbar}{2m^2}\sum_{i \neq n}\frac{\boldsymbol{P}_{n,i}(\boldsymbol{k}) \times \boldsymbol{P}_{i,n}(\boldsymbol{k})}{E_n^0(\boldsymbol{k}) - E_i^0(\boldsymbol{k})}$$

Finite **m** is responsible for the anomalous g factor of electrons in semiconductors, which manifests itself in a shift of Zeeman energy in the presence of a magnetic field.

The existence of finite orbital magnetic moment also suggests that the valley carriers will possess optical circular dichroism, i.e., they will exhibit different properties upon illumination with right- or left-circularly polarized light.[9-11] Though optical circular dichroism is also present in systems with broken time-reversal symmetry, it should be understood that the underlying physics in valleytronic materials is quite different and the dichroism is present even when time-reversal symmetry is maintained. One effect of the orbital magnetic moment are valley optical selection rules.[8]

As a specific example, the 2H phase of many 2D transition metal dichalcogenides lack inversion symmetry and as a result exhibit contrasting **Ω** and **m** between the K and K' valleys. The $\boldsymbol{k} \cdot \boldsymbol{p}$ Hamiltonian at the band edges in the vicinity of K and K' is given by:

$$\hat{H} = at(\tau_z k_x \sigma_x + k_y \sigma_y) + \frac{\Delta}{2}\sigma_z$$

Where a is the lattice spacing, t is the nearest neighbor hopping integral, $\tau_z = \pm 1$ is the valley index, σ is the Pauli matrix element, and Δ is the bandgap. In this case the Berry curvature in the conduction band is given by

$$\boldsymbol{\Omega}_c(k) = -\hat{\boldsymbol{z}}\frac{2a^2t^2\Delta}{(4a^2t^2k^2 + \Delta^2)^{3/2}}\tau_z$$

Because of the finite Berry curvature with opposite signs in the two valleys, an in-plane electric field induces a Valley Hall Effect for the carriers, see Figure 3. Note that the Berry curvature in the valence band is equal to that in the conduction band but with opposite sign.

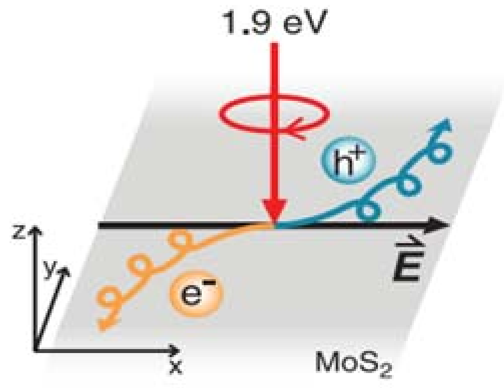

Figure 3: Anomalous motion perpendicular to an applied magnetic field (Valley Hall Effect) caused by finite and contrasting Berry curvature. From reference [12].

The orbital magnetic moment has identical values in the valance and conduction bands:

$$\boldsymbol{m}(k) = -\hat{\boldsymbol{z}}\frac{2a^2t^2\Delta}{4a^2t^2k^2+\Delta^2}\frac{e}{2\hbar}\tau_z$$

Non-zero **m** implies that the valleys have contrasting magnetic moments (through $\tau_z = \pm 1$) and thus it is possible to detect valley polarization through a magnetic signature. The orbital magnetic moment also gives rise to the circularly polarized optical selection rules for interband transitions. The Berry curvature, orbital magnetic moment, and optical circular dichroism η(**k**) are related by

$$\eta(\boldsymbol{k}) = -\frac{\boldsymbol{m}(\boldsymbol{k})\cdot\hat{\boldsymbol{z}}}{\mu_B^*(\boldsymbol{k})} = -\frac{\boldsymbol{\Omega}(\boldsymbol{k})\cdot\hat{\boldsymbol{z}}}{\mu_B^*(\boldsymbol{k})}\frac{e}{2\hbar}\Delta(\boldsymbol{k})$$

Where $\mu_B^* = e\hbar/2m^*$ and $\Delta(\boldsymbol{k}) = (4a^2t^2k^2+\Delta^2)^{1/2}$ is the direct transition energy, or bandgap, at **k**. Exactly at the energetic minimum K and K' points where the kinetic energy (and thus momentum) equals zero, we have full selectivity with $\eta(\boldsymbol{k}) = -\tau_z$. The transition at K couples only to σ^+ light and the transition at K' couples only to σ^-. This selectivity allows the optical preparation, control, and detection of valley polarization (Figure 4).

In summary, if the Berry curvature has different values at the K and K' points one can expect different electron, hole, or exciton behavior in each valley as a function of an applied electric field. If the orbital magnetic moment has different values at the K and K' points one can expect different behavior in each valley as a function of an applied magnetic field. Contrasting values of **Ω** and **m** at the K and K' points give rise to optical circular dichroism between the two valleys which allows selective excitation through photons of right- or left- helicity. In order to have contrasting values of **Ω** and **m** while maintaining time reversal symmetry it is necessary that the material exhibit a lack of spatial inversion symmetry. Though spatial inversion symmetry can be induced in gapped graphene, for example by biasing the substrate underlying bilayer graphene, monolayer 2D transition metal dichalcogenides meet this requirement without the need to externally introduce a band gap or symmetry breaking, and thus TMDs appear to be the most promising candidates for useful valleytronic applications.

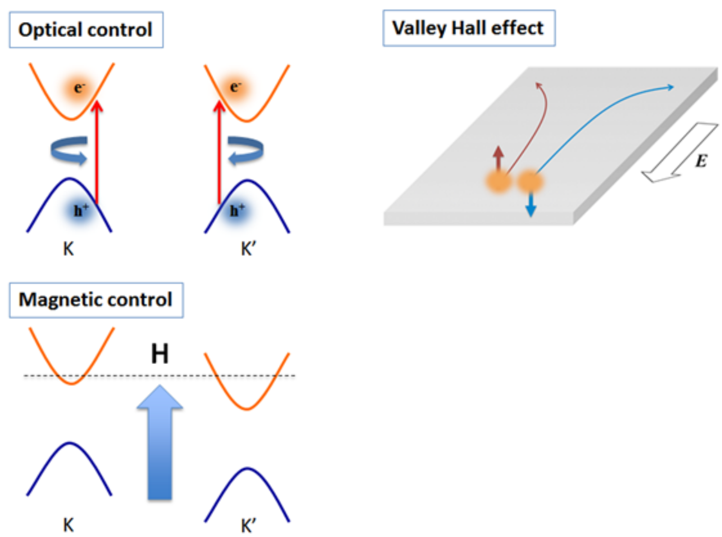

Figure 4: Three methods of control of the valley state: optical, electrostatic, and magnetic. Courtesy Kin Fai Mak.

6. BREAKOUT SESSIONS

This section consolidates the major findings and constitutes the most important output of the workshop. The three subsections below correspond to the three topic areas which were discussed during the breakout sessions. We begin with an analysis of the basic physics associated with valleytronics, including what we know and what need to know. The next subsection describes the opportunities or applications which can be enabled by the physics unique to valleytronics. The last subsection dives into the details of improvements in valleytronic material quality and device technologies which will be required to make valleytronics practical.

6.1 CURRENT STATE OF KNOWLEDGE

In this section we consider what has been learned about valleytronics and what are the remaining unanswered physics questions. The unique physics of valleytronic materials stems from lack of inversion symmetry and the ability to address individual valleys by optical, magnetic, or electric fields. In fact, these defining characteristics may be used to distinguish valleytronic materials from other materials which exhibit minima in the band structure. The consensus of the group was that the first-order physics models associated with recently observed phenomena such as the Valley Hall Effect [12] are sufficiently understood. However, valleytronics is a new field and many physics questions have not yet been posed let alone answered.

6.1.1 Valley Coherence, Manipulation, and Transport

Valley lifetime and coherence are critically important to useful information processing applications, as any device which relies upon polarized valley populations will only be useful for as long as that valley polarization persists. Note that there is sometimes confusion between the terms lifetime and coherence; we will use “valley lifetime” or “valley polarization” to mean how long a population of electrons, holes, or excitons remains in the K or K' valley before scattering to the opposite valley. “Valley coherence” is reserved for discussing the phase relationship between a particle in a superposition of two different valleys, such as that induced by linearly polarized light,[13] or between two separate particles.

Figure 5 shows the valley lifetime of excitons, trions, electrons, and holes across several different TMDs as measured by circularly polarized photoluminescence and Kerr rotation techniques by various research groups.[10, 14-30] Most of this data was taken at low temperature (~ 4 K). Details are available in the references but the overall trend is immediately clear. The valley lifetime of excitons (0.1 – 100 ps), trions (0.1 – 1 ns), electrons (1 – 100 ns), and holes (> 100 ns) are clearly different. Note that the valley lifetime can be shorter or longer than the recombination lifetime of the species. If the valley lifetime is long compared to the recombination lifetime, near-unity valley polarization of the emitted photoluminescence is expected. If the valley lifetime if short compared to the recombination lifetime, a small polarization signal would be expected. For practical applications both the valley lifetime and the recombination lifetime would need to be as long as possible, so electrons and holes may be more useful than excitons or trions.

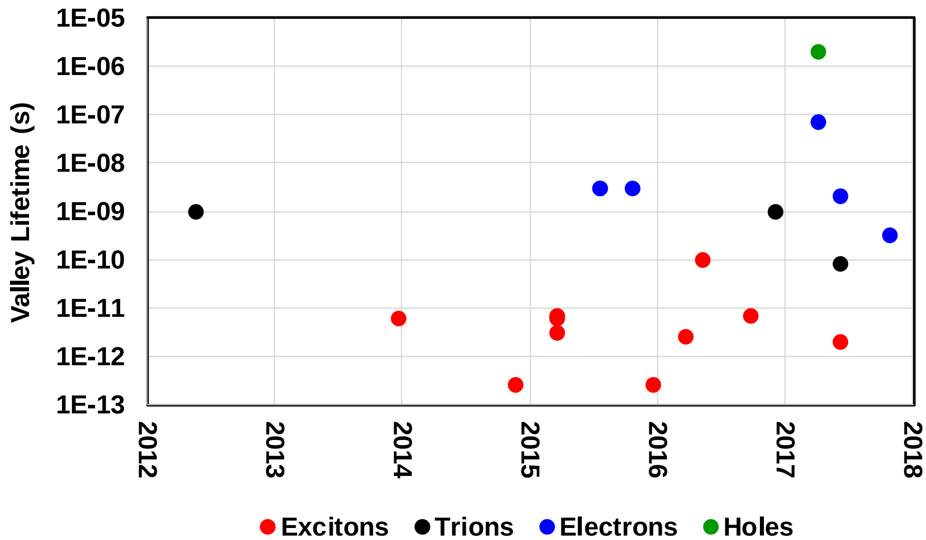

Figure 5: Valley polarization lifetime as a function of publication year for excitons, trions, electrons and holes in various monolayer TMDs.

To achieve a practical application one must be able to perform some manipulation of the valley state within its lifetime. Though it is known how to create a valley exciton state at any point on the Bloch sphere using circular, linear, or elliptically polarized light, it is not clear how one can perform an arbitrary rotation from one state to any other state on the sphere. Manipulations have been shown in limited cases.[25, 31] Using linearly polarized light one can create a superposition state $\frac{1}{\sqrt{2}}\left(|K\rangle + e^{-i\omega t}|K'\rangle\right)$ on the equator of the sphere. ω is proportional to the energy difference been the two valleys. Breaking the degeneracy between the K and K' states by DC magnetic or AC electric fields will cause the phase to evolve differently in the two states thus effecting motion along the equator (Figure 6). By contrast, rotating a state in the orthogonal direction, that is to say a π rotation from one pole to another has yet to be realized. Demonstrating arbitrary valley state rotations and developing valley analogs of NMR and spin echo techniques would be preliminary steps toward systems which exploit controlled valley manipulation.

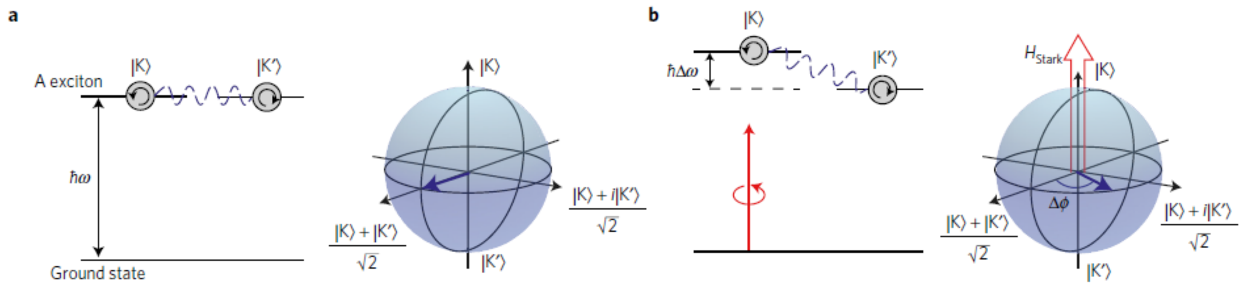

Figure 6: Representations of the Valley state on the Bloch sphere. A coherent superposition of K and K' states (left). Lifting the degeneracy between states induces motion of the state around the equator (right). From reference [31].

Zeeman splitting in these materials is very weak, about 0.2 meV/T, which means that extremely high magnetic fields would be necessary to perform a state rotation within the valley lifetime. However, it has been shown that breaking of time reversal symmetry through the optical Stark Effect (which can induce an effective magnetic field of at least 60 T) can be observed without any applied magnetic fields.[32] Additionally, heterostructures of semiconducting TMDs on top of magnetic materials have also shown very high effective fields, such as with WSe_2 on CrI_3 (Figure 7). Other options for creative means to break time reversal symmetry should be explored.

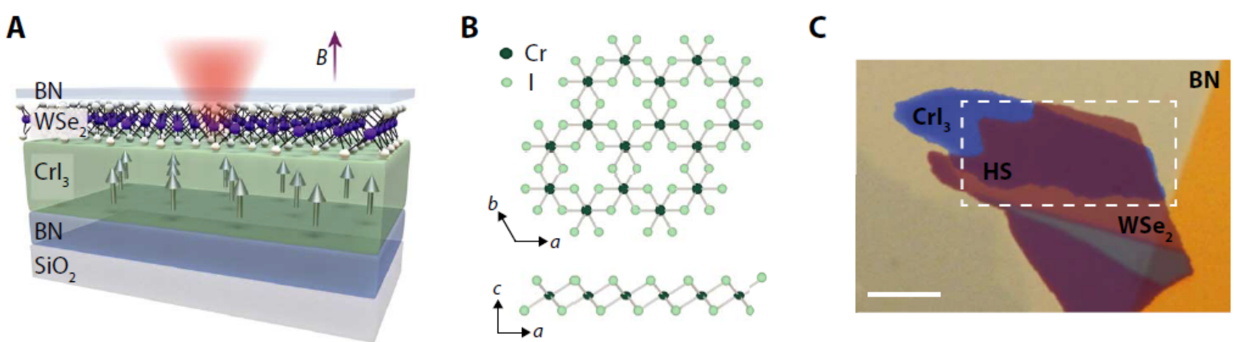

Figure 7: Heterostructure of WSe_2 on CrI_3 from reference [33].

For valleytronics to be useful, we must also understand the physics of valley transport across a crystalline domain, across domain boundaries, and even between different materials. The physics of valley transport is not well established and needs study, perhaps through pump-probe experiments with spatially delocalized pump and probe beams.

6.1.2 Exciton Valley Lifetime and Coherence

Here we consider exciton populations in some more detail as the majority of experimental measurements to date have been on excitons due to the relative simplicity of photoluminescence experiments. Valley lifetime for excitons in monolayer 2D TMDs is quite short, about 1 ps. The recombination lifetime is longer, about 10 ps. Thus exciton recombination is not the limiting factor for valley polarization. The dominant mechanism for loss of valley polarization is not firmly established. One theory is that the loss is dominated by the exciton exchange interaction where annihilation of an exciton in one valley is accompanied by the formation of an exciton in the opposite valley. If that is the case, then it may be very difficult to construct a useful device based on simple excitons as it is not clear that there is any practical way to discourage this exchange interaction and prolong valley lifetime.

There is evidence that dark exciton valley lifetime may be much longer, on the order of 100's of picoseconds. Dark excitons are bound electron-hole pairs where the electron and hole have equal spin. This situation can occur when splitting of the conduction band by spin-orbit coupling is more pronounced, and the VB maximum is of opposite spin to the CB minimum. Typically, if a spin-up electron is promoted to the conduction band, it leaves behind a spin-down hole thus preserving spin conservation. If conduction band splitting is large, and the spin-down state is lower, it would be energetically favorable for the spin-up electron to relax to the lowest conduction band even though that would entail a spin flip. One is left with a spin-down electron and a spin-down hole. Since exciton recombination is spin-forbidden in this case, photoluminescence is not observed and the exciton is termed “dark”. In MoX_2 TMDs the conduction band splitting is quite small, and dark excitons are not expected. In WX_2 TMDs the conduction band splitting is on the order of 30 meV, and dark excitons are possible. In addition to the long dark exciton recombination lifetime, it was suggested that the exciton exchange interaction is forbidden for dark excitons, thus explaining the longer dark exciton valley lifetime. It is an open question whether coherent superposition or manipulation of dark excitons is possible. Similar arguments can be made about trions (an exciton with an extra electron or hole) as well.

Indirect excitons, where the hole is in one layer and the electron is in the other layer of a heterogeneous bilayer stack of 2D materials, exhibit much longer lifetimes on the order of 100 ns. Similar to the argument above for dark excitons, it has been conjectured that indirect excitons are protected against the exchange interaction. Indirect excitons have the advantage of being bright as opposed to dark, that is to say the oscillator strength is large and they are much more easily seen in photoluminescence experiments and presumably are easier to manipulate with light as well.

In cases where valley lifetime is determined by some extrinsic factor (as opposed to the exchange interaction) there is the potential to mitigate the loss mechanisms. For example, if scattering off impurities or defects is the dominant mechanism in loss of valley polarization, it should be possible to increase valley lifetime by reducing defect density. Thus understanding the mechanisms of depolarization is critically important. The effect of phonons, disorder, and nuclear spins on valley lifetime has not yet been the subject of study. Additionally, there are open questions on the effect of reduced dimensionality as it is possible that 0D or 1D systems will exhibit more favorable lifetime properties.

Compared to valley lifetime, exciton valley coherence time has been scarcely considered in the literature. Though coherence has been observed through linearly polarized photoluminescence, we are aware of only two published measurements of valley coherence time.[25, 31] These suggest an exciton valley coherence time, or T_2*, of less than 1 ps. More work is needed in this area.

6.1.3 Free Carrier Valley Lifetime and Coherence

Although data is more scarce than for excitons, valley lifetimes for free carriers have been measured and appear to be much longer than for excitons, as long as 2 μs for holes (Figure 8), and somewhat less for electrons. It is believed that the lifetime is shorter for electrons because the smaller SOC in the conduction band results in less spin-protection of the valley state. It is likely that electron and hole valley lifetimes are much longer than for excitons because the exchange interaction is not available for free carriers. Additionally, the lifetime of the free carriers themselves should be long compared to that of strongly-bound excitons. Still, electron and hole depolarization mechanisms must be understood to maximize free carrier valley lifetime.

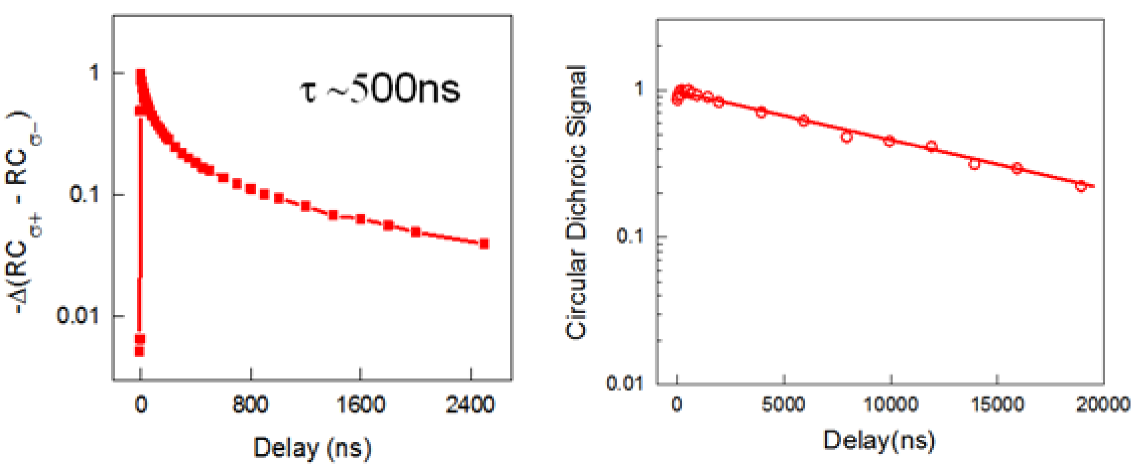

Figure 8: Long hole valley lifetime measured in intrinsic (left) and hole-doped (right) WS_2/WSe_2 heterostructures. Courtesy Feng Wang.

Switching now to valley coherence, it is not completely clear if quantum coherence between valley states is even possible when applied to free carriers. Crystal momentum is a continuous variable, and any small perturbation of an electron or hole from the minimum energy state may destroy coherence. Excitons, by contrast, exhibit one tightly bound state for each region in momentum space.

Thus excitons have the advantage of demonstrated coherence, but electrons and holes have the advantage of longer valley lifetime. So it may be that excitons are of more utility than free carriers for quantum information applications. On the other hand, since excitons are neutral species they are difficult to transport. Trions may be able to satisfy the need for both coherence and transport. Alternatively, transferring valley information from excitons to free carriers to satisfy both coherent manipulations and transport needs may be required.

6.1.4 Other Physics Topics

The surrounding materials will have a significant impact on valley properties. For example, some substrate materials are known to quench photoluminescence. By contrast, inserting a layer of hBN between TMD layers makes indirect exciton lifetime longer. Designing a suitable substrate which will not interfere with valleytronic properties, or which may even enhance valleytronic properties, would be an exciting topic for computational materials science.

For a given monolayer of TMD material, the conductivity due to the Valley Hall Effect (VHE) cannot be easily tuned, and its magnitude is intrinsically linked to the doping level. It is difficult to turn on and off the VHE, as one would want do with a valleytronic switch. In bilayer TMDs, the VHE is absent as inversion symmetry is restored. If one could switch between a monolayer and bilayer state, the VHE and the associated valley conductivity could be turned on and off. In fact, electrostatic gating of bilayer TMDs induces some degree of symmetry breaking, in effect switching between a bilayer and two un-interacting monolayers. The strong dependence of both the magnitude and polarity of the Valley Hall conductivity on the applied field presents a way to electrically tune the VHE in bilayer TMDs, and thus bilayers of TMDs may be useful for selective valleytronic transport.

Bilayers of stacked 2D materials (Figure 9) provide an additional rotational degree of freedom to control valleytronic effects as well. The moiré patterns in stacked TMD bilayers produce periodic potential wells as deep as 160 meV. These may be useful for creating quasi-atomic lattices of particles which can be employed as arrays of devices for memory or logic operations. It is known that exciton-polaritons can condense into a BEC. If the BECs at given lattice points in the moiré pattern can be made to interact, it may be possible to realize the BEC equivalent of an atom interferometer.

On another note, the physics of valley superconductivity has not been explored. Though superconductivity in 2D materials has been demonstrated, valley-polarized superconductivity has not been addressed. Normally Cooper pairs would consist of electrons from opposite valleys, but in valleytronic materials the Cooper pairing may be quite unusual. Is it possible to create a new superconducting quasiparticle with electrons from the same valley? 2D superconductivity at low electron density as well as superconductivity in Landau Levels has not yet been studied.

Finally, it should be noted that valleys other than K/K' do exist in these materials, such as at the Γ and Q/Q' points. Though these valleys do not represent global energetic minima, one should investigate if there are interesting valleytronic properties at these points.

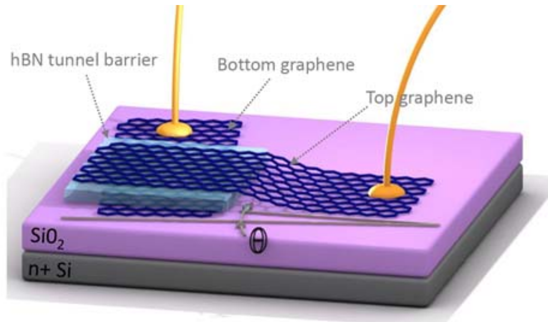

Figure 9: Twisted bilayers of graphene show valley-dependent effects based on the twist angle. Courtesy Artem Mishchenko.

6.2 EMERGING OPPORTUNITIES

In this section we consider what are the most promising applications for valleytronics and what are the big technical challenges to realize these applications. It is immediately apparent that no “killer app” for valleytronics has yet been identified. The focus of the research to date has been on material growth, characterization, and valley physics experiments, without extensive consideration of practical devices or systems based on the valleytronic properties of these materials. So it was very important to take time in this workshop to discuss what are the useful technology implications of valleytronics.

6.2.1 Information Processing

We considered valleytronic information processing in both the quantum domain (e.g., as an alternative to superconducting qubits or trapped ion qubits), and the classical domain (e.g., as a supplement to or replacement for silicon).

In principle one could perform quantum gate operations on the valley pseudospin of excitons, electrons, or holes. As described above, there are tradeoffs between the lifetime and the ease of performing quantum operations with each of these species. It is not clear at this time whether excitons, electrons or holes would be the preferred storage medium for quantum information. More work needs to be done to explore these options. Note that the quantum basis need not be composed of just a single particle, say an exciton, in |K⟩ or |K'⟩. One could employ two entangled excitons with a controlled coupling between them using singlet = $\frac{1}{\sqrt{2}}(|KK'\rangle - |K'K\rangle)$ and triplet = $\frac{1}{\sqrt{2}}(|KK'\rangle + |K'K\rangle)$ states as the basis. For electrons and holes, the real spin is also available for quantum information storage. One could conceive of a more complicated basis set comprised of $[|\uparrow_K\rangle, |\uparrow_{-K}\rangle, |\downarrow_K\rangle, |\downarrow_{-K}\rangle]$. This would require the technology to perform manipulations on both the real spin and the valley pseudospin but may hold some computational advantage.

Using the TMDs as qubits for quantum computing has some very attractive potential benefits. It may be significantly easier to integrate thousands or millions of valley qubits on a layer of TMD in a simple planar architecture as compared to other modalities such as trapped ions. Because spin-orbit coupling provides energy separation between ↑,↓ states, and the valley index provides momentum separation between K, K' states, each quantum index provides a degree of protection of the other index. So spin protection of valley or valley protection of spin may provide longer coherence times than other unprotected qubit candidates. Because valley qubits are interrogated at optical instead of microwave frequencies, single qubits could be addressed through submicron waveguides allowing a much higher density of qubit packing compared to that for superconducting qubits, which are limited by microwave transmission lines and inductors. Gate operation times may be concurrently faster as well. On the other hand, there is the notable concern that large the spin-orbit coupling will increase the interactions between the valley qubit and its environment, thus reducing coherence time. This underscores the importance of measuring and understanding the decoherence mechanisms of the valley states.

Transistors for classical computation is the canonical application for semiconductor materials and it is natural to explore whether a new class of semiconductors such as TMDs will enable a better transistor. It is apparent that the unique physics of valleytronic materials offer a new computational degree of freedom beyond charge. In spite of this, a specific enablement of a valleytronic computational element that provides a real-world advantage over silicon CMOS has not yet been proposed. Thus the most urgent technical challenge in this space is to identify a viable valleytronic logic or memory device design.

It should be emphasized that valleytronics is not another subtle variation of spintronics. The physics underlying spin-based and valley-based computing are completely different. Most proposed spintronic devices require conventional charge transport for switching operations, though with some enhancement of their retention or on/off ratio characteristics provided by a conductivity difference between spin-up and spin-down electrons through a magnetic material. Spintronic devices have yet to demonstrate meaningful power or performance advantage compared to conventional silicon CMOS, as the thermodynamic switching limitations are similar. Valleytronic switches, by contrast, take advantage of unique light-matter interactions and/or evolution of the phase difference between particles in the K and K' valleys. The energy scale for these operations will be governed by the splitting induced between the valleys, which maybe on the order of 30 meV or about 30x lower than commercial silicon CMOS technology. Since the device switching energy (in conventional transistors) scales quadratically with voltage, this would translate to a 1000x reduction in power required.

Though an all-valleytronic computational element is perhaps the most forward-thinking opportunity, one must also consider how valleytronics can enhance existing computational devices. By taking advantage of spin-orbit coupling, for example, valleytronic components may make spin-logic devices more attractive. Existing spin-logic device concepts require magnetic fields or relatively large currents to switch from an "on" to an "off" state. Because of this, spin-logic devices are either slow, or power-hungry, or both. Thus in spite of determined effort over the past two decades, spin-logic devices are not widely seen as viable replacements for or complementary to silicon CMOS. But by coupling spin-logic architectures with valleytronic materials it may be possible to eliminate the need for magnetic fields or large currents. If spin polarized currents of either polarity can be efficiently generated in the valleytronic material, the spintronic material could be used as a filter. The switching energy and switching speed would be governed by the operations on the valleytronic material. Note that valley-protection of spin could increase the spin lifetime and mean free path which are important for information storage and transport.

6.2.2 Other Applications

Developing a valleytronic computational technology which meets or exceeds the current state of the art with respect to performance, power, reliability and cost will be a long term effort. It is also useful to consider applications with less complexity that can be realized quickly, even if the impact is less broad. One compelling idea is to use valleytronic effects to develop non-reciprocal optics such as an integrated photonic optical isolator. Optical isolators are a long-awaited missing component in the integrated photonics toolbox. The inherent optical dichroism of valleytronic materials along with the means to address individual valleys through breaking time reversal symmetry suggest that these materials could be ideally suited to form a microphotonic optical isolator. It may even be possible to construct a gated isolator that switches direction based the handedness of a valley current.

One could also take advantage of the optoelectronic properties of valleytronic materials to make polarization sensitive detectors. Polarization sensitive optical detection can provide significant operational advantages, including differentiating man-made objects from natural background clutter and generating high-resolution 3D reconstructions from limited data. Full-Stokes polarimeters measure all four components of the Stokes vector, allowing reconstruction of the polarization of the incoming light whether it is circular, linear, or elliptical. Full-Stokes polarimeters have been demonstrated using mechanically rotated optical filters and liquid crystal-based variable retarders. However, these systems are slow to rotate between different polarizations which causes loss of resolution due to scene movement between image captures. An intrinsically polarization-sensitive detector capable of operating at fast frame rates with no moving parts would open new capabilities for space-based imaging and ranging as well as terrestrial applications. But there are no commercial photodetectors which are inherently capable of discriminating between left, right, and linearly polarized light, as would be possible with detectors made from valleytronic materials. Technical challenges in this area include improving the efficiency of light absorption and quantifying the ability to discriminate between light of different polarizations.

Along similar lines, one could develop photon emitters which dynamically switch polarization based on electrical inputs. This could improve the efficiency of single photon emitters for Quantum Key Distribution or quantum repeaters for long-haul quantum communications. The fidelity of polarized light emission and improvements in quantum efficiency are technical challenges which merit further evaluation.

6.3 MATERIAL AND DEVICE NEEDS

In this section we consider what improvements in valleytronic materials, process technologies, and device designs the community needs to make in order to bring forth useful systems which take advantage of valleytronic properties.

6.3.1 Domain Size and Grain Boundaries

Valleytronic properties are predicated upon the solid state physics of an ideal single crystal. By contrast, an amorphous film of MoS_2 presumably will not exhibit any useful valleytronic effect. In the absence of data to the contrary, we assume that ideal valleytronic effects will be observed only if the entire active area of the device or circuit is composed of a single crystalline domain. Polycrystalline material may exhibit some degree of valleytronic behavior within each small crystalline domain, but valleytronic information will likely be lost if the macroscopic area of the device is comprised of multiple small domains in different orientations. Valley information transport across a disordered grain boundary may be inefficient or even impossible.

So how does one address this issue? Ideally by having a single crystalline domain across an entire substrate as is the case with commercial electronic products fabricated on single crystal wafers (e.g., Si, SiGe, GaAs, GaN, SiC, or InP). With bulk materials such as these conventional semiconductors, essentially perfect crystallinity across a wide area is readily achieved by growth from a melt or by homoepitaxy. Unfortunately, it is not possible to grow a single monolayer of MoS_2 (or any TMD) from a melt, and clearly homoepitaxy is not consistent with isolating a monolayer. High quality single-crystal films of bulk semiconductors can also be grown through heteroepitaxy, though it requires a succession of strain release layers to gradually improve the lattice matching between the substrate and the desired material. It appears upon initial inspection that large-area single-crystal TMD growth could be performed the same way. However, it is critical to keep in mind that valleytronic effects require *a single monolayer* of TMD. Heteroepitaxy of a bulk material, such as GaN, does not begin with an even surface coverage of a single atomic layer of material. The first few Angstroms of GaN "puddle-up" into islands which do not coalesce into a continuous film until some nanometers of thickness is achieved. Fortunately, these islands are registered to the underlying strain-relief layer, so as the material grows thicker these early-growth domain boundaries disappear and one is left with a uniform single-crystal film after some thickness. Clearly this approach will not work when a single monolayer is needed.

This is a significant problem. There is a large and growing literature on growing monolayer TMDs by VPT, VPE, CVD, ALD, and MBE on different substrates including Si, SiO_2, sapphire, graphene, and hBN. All of these approaches are essentially trying to perform monolayer heteroepitaxy. The results of these attempts are all broadly similar. Although "large-area growth" is frequently reported, the material is far from the wafer-sized single crystal that one might envision. Domain sizes range from 10's of nm to 10's of microns. Frequently the material does not form a continuous film at all, but instead consists of a sparse scattering of isolated micron-sized single crystals. Indeed, one of the most time consuming parts of this work is to search across the sample for a "publication worthy" flake upon which to perform spectroscopic analysis or device fabrication. In the cases where the film is continuous, the material is polycrystalline with domains which are not registered to one another and are separated by highly disordered grain boundaries.

Development of a synthesis technique for large (10's of mm) single crystal domains of monolayer TMD material is essential for developing real systems which exploit valleytronic behavior. Projects to explore adapting conventional heteroepitaxy to monolayer TMD growth will provide valuable insight into whether it is feasible to grow large area single-crystal TMDs by this technique. Alternatively, one could explore increased domain size through homoepitaxy, for example by growing on top of exfoliated flakes or bulk geological material, along with a means to cleanly separate the newly-grown monolayer. Liquid phase synthesis should be considered as well. In the end, there may be fundamental or practical limitations to monolayer TMD domain size, such as the width of the atomic layer terraces of the underlying substrate which must be understood. Theoretical study of the thermodynamics of monolayer TMD formation over these length scales may be very insightful.

6.3.2 Defect Reduction

Large single crystals of even common commercial materials are of course not defect-free, and in the case of valleytronic material random defects will be detrimental to the valleytronic properties. A valleytronic device will be reliant on some persistent population of electrons, holes, or excitons in those valleys, so the valley lifetime of a material is a critical property. In addition to persistence, useful devices may need to transport electrons, holes, or excitons from one spatial location to another without undue loss of valley information. This implies that valley mean free path or valley scattering length will also be very important. Therefore, when we speak of "valleytronic-quality" material we mean that the material possesses sufficient valley lifetime and mean free path to perform its intended function.

Although the community is still in the early stages of understanding this topic, it is probable that vacancies, substitutions, and extended defects will all adversely affect valleytronic properties. The role of some donor defects such as chalcogen vacancies or excess metal atoms and some acceptor defects such as metal vacancies or excess chalcogen atoms is beginning to be explored. Further study of these and other defect types to understand the quantitative impact on valleytronic properties is very important.

One then turns to defect reduction. Within the small domains of single crystal TMD flakes described above, the defect density of TMDs such as MoS_2 grown by VPT or CVD is about 10^{13} cm^{-2}. This is roughly 10,000x higher than the defect density in microelectronic-grade silicon. Better understanding of the kinetics of TMD growth by various means should result in reduction of defect density. Defect healing of TMD material, such as by annealing of exfoliated flakes in chalcogen or other ambient followed by correlated measurements of defect density and valleytronic properties, should be pursued. In this case, exfoliated material could be employed as a short-term solution as the results will likely transfer to grown material as it improves.

But what defect density is good enough? This cannot yet be answered as we do not yet have a direct correlation between defect density and valleytronic properties, and we do not yet know the fault tolerance of valleytronic devices. It has been proposed that valley polarization is linearly proportional to the defect density for very high levels of defects, but that is likely an optimistic scenario when extrapolated to low defect densities. Monolayer 2D TMDs are still a relatively new class of materials, and one aspect which has not yet been studied is what are the theoretical minimum limits of defect density. An effort to determine the thermodynamic limits of defect density, combined with the effect of those defects on valley lifetime and mean free path, would provide very compelling evidence on the ultimate performance limits of valleytronic materials. Experimentally, it is recommended that the community engage in materials benchmarking and standardization to produce valleytronic-quality materials with defined properties which include defect density and type(s), carrier concentration, carrier mobility, and photoluminescence. These will serve as proxies for the more impactful (and much more difficult to measure) properties of valley lifetime and mean free path.

6.3.3 Other Materials Issues

Interface quality is extremely important when working with 2D materials. Heterostructures of different materials including TMDs, hBN, and graphene (Figure 10 and Figure 11) have been shown to exhibit improved properties, such as higher mobility, compared to simple single layer TMDs in direct contact with a bulk substrate. Good contacts to monolayer TMDs are extremely sensitive to the surface condition, with contact resistance decreasing as one moves to high vacuum and ultra-high vacuum metal deposition processes. Multilayer stacking of materials (Figure 12) provide insight into the influence of interfaces, contamination, and layer alignment on valleytronic properties. Current methods for multilayer stacking are time-intensive, labor-intensive, and low-yield. Simple and reproducible recipes for cleaning and preparing atomically sharp interfaces are desired.

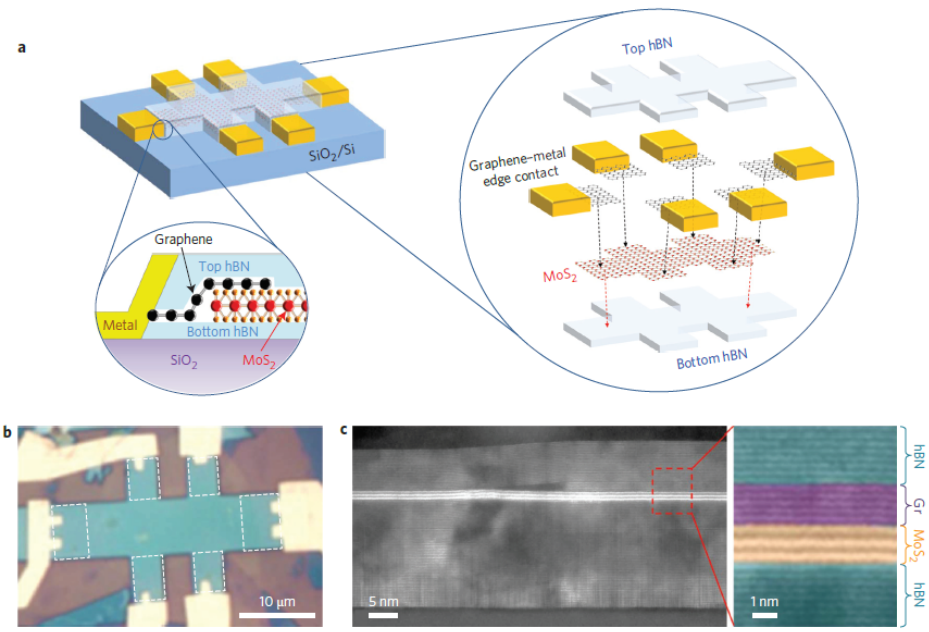

Figure 10: High mobility measurement of MoS_2 enabled by heterostructure formation. From reference [34].

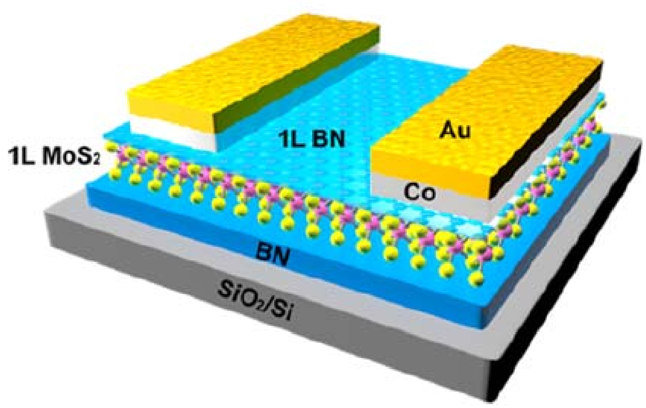

Figure 11: Complex metal stack required for good ohmic contact to MoS_2. From reference [35].

The dopant density in these materials must be better controlled, and eventually the dopant density must be tunable based on the device needs. Currently, material grown in different laboratories exhibits widely varying dopant density. In some cases, a given TMD can even exhibit n-type or p-type behavior as a result of differences in sample preparation. It is likely that the substrate material, process cleanliness, and other subtle variables are important here. Maturation of growth processes and protocols is necessary to control dopant density.

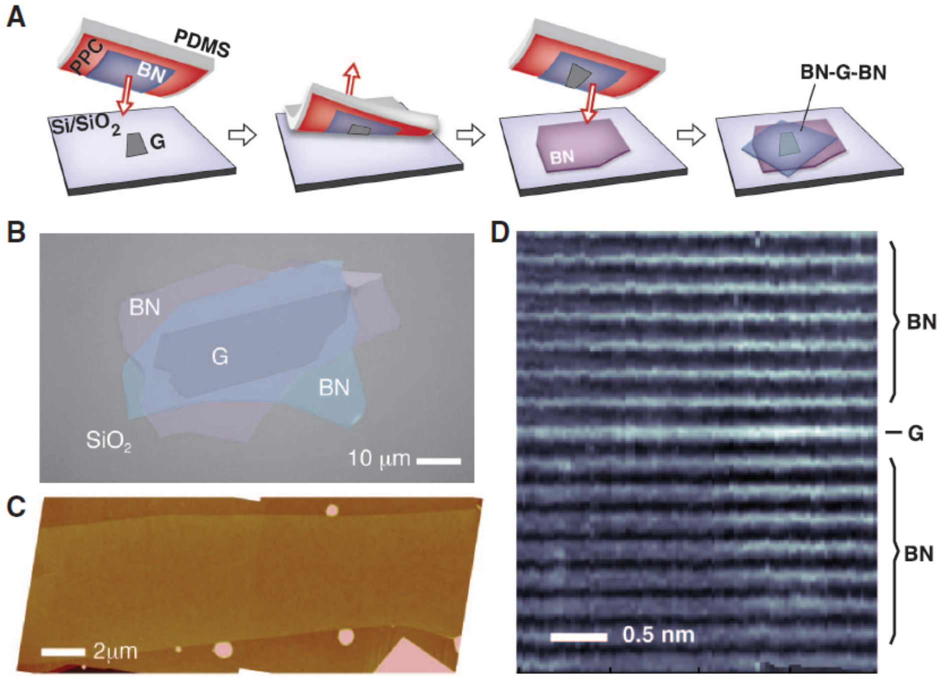

Figure 12: BN/graphene/BN heterostructures fabricated by stamping. From reference [36].

6.3.4 New Materials

The list of 2D materials which have been experimentally realized continues to grow. From a valleytronics perspective, not all of these new 2D materials are clearly useful. 2D materials with improved valley lifetime and mean free path are definitely needed. Synthesis of such material by trial and error is likely to be very labor intensive, especially as one begins to consider binary and ternary alloys. A materials modeling effort to design the next generation of valleytronic material would be extremely valuable. Basic questions remain unclear, such as: Will alloys of TMDs retain (or enhance) valleytronic properties? Can we design 2D materials with larger spin orbit coupling and thus greater spin protection of the valley state?

Or can we design materials with significant spin orbit coupling in the conduction band as well as the valance band?

One can also look for design principles to guide development of new valleytronic materials. For example, are there trends among the chalcogens (S, Se, Te) to guide us? Or is valleytronics practical in another class of materials beyond 2D hexagonal honeycomb lattices? The community would benefit from a concerted effort in computational materials design to optimize valleytronic properties, starting with TMDs and other van der Waals layered materials and extending to novel low-dimensional heterostructures such as oxides, nitrides and mixed phases.

It would be useful to form a materials database to combine data from modeling and experimental results focusing on valleytronic properties. Conceivably one could then use machine learning or other data mining techniques to discover promising paths for future material development.

6.3.5 Valleytronic Devices

There are cases where a theoretical device concept drove the development of new materials (e.g., spintronics) and there are many cases where the discovery of new materials eventually led to the development of a new device (e.g., giant magnetoresistance materials). Valleytronics is clearly in the latter category; we assert that there have been no valleytronic device concepts yet published which convincingly promise performance advantages in practical systems. This is a critical gap in the argument for valleytronics as a technology element as opposed to an interesting physics phenomenon. The previous section provided several high-level ideas for valleytronic information processing and optoelectronic elements. But fully-developed concepts of how one would actually realize such devices is lacking. Efforts to rectify this situation should be given the highest priority.

Though we should not at this stage limit the creativity of investigators to come up with new valleytronic devices concepts, there are several emerging device ideas which are of interest to the user community. The first are we consider are logic devices which use valleytronic information to gain some advantage over classical MOSFETs. This could include using valley polarizability to enable a sub 60 mV/decade electrical switch, using valley-protection to enable robust room-temperature spin-based computing, or using the momentum index itself to perform computation. A FET-like device concept using a graphene nanoribbon approach has been proposed (Figure 13). This device uses the Rashba effect to induce a phase difference between the electron wavefunctions in the K and K' valleys. As the physics mechanism for turning off the device is significantly different from that of a conventional MOSFET, 60 mV/decade may no longer limit the operating voltage. Though the proposed device employed graphene, TMDs may be more advantageous. Another approach is to use engineered defects as part of a valley-filter device. At a line defect, it has been shown that asymmetric wavefunctions in these materials go to zero, so the density of states goes to zero and thus transmission equals zero. By contrast for symmetric states transmission is 1. Therefore valley polarization could be induced by using line defects as a filter.[37]

Alternatively line defects could be used as physical barriers, to confine valley transport between two parallel defects.

Valley polarized currents have been demonstrated in Hall bar structures, see Figure 14. Integration of such a valley-polarized current source with valley-FETs, valley-filters, or spintronic elements will start to build the device toolbox necessary to generate logic gates. In addition, by finding ways to extend the length of these valley-polarized currents through improved material quality, valley amplifiers, or other means, one can then start to build valley-interconnects between devices.

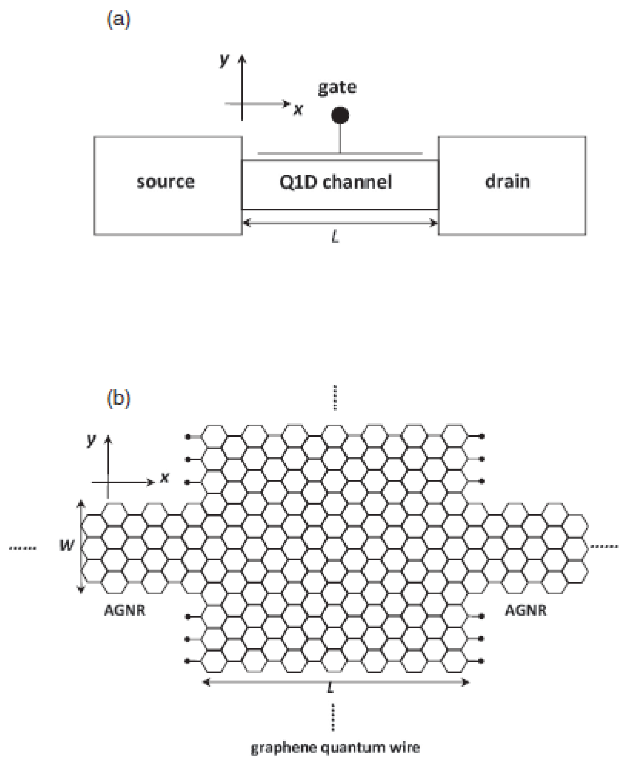

Figure 13: Concept for a valleytronic transistor based on the evolution of the phase of the K and K' states between the source and drain. From reference [38].

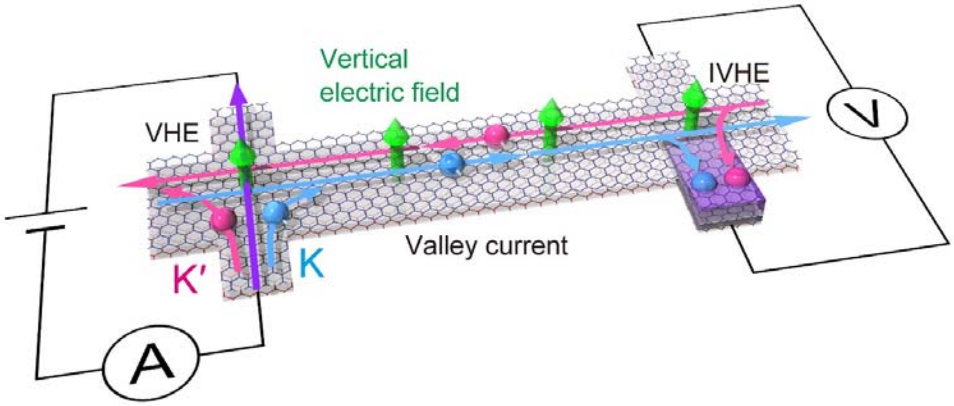

Figure 14: Device for valley polarized current transport. From reference [39].

The second fruitful device area comprises quantum computing elements. For example, a qubit architecture composed of two graphene quantum dots has been proposed (Figure 15). The orientation of the valley pseudospin in each quantum dot places the qubit into a singlet or triplet state. The pseudospin in each quantum dot is rotated by an in-plane E-field between two parallel gates, and a control gate between the two quantum dots controls the coupling between them. The qubit can rotate from "North" to "South" on the Bloch sphere by changing the direction of an individual pseudospin, and motion around the equator is effected by allowing tunneling or an exchange interaction between the two quantum dots modulated by a control gate.

A third device technology area is microphotonic elements. Devices for chiral light emission or detection with power or performance advantage over existing commercial technologies can be envisioned, for example spin-lasers, polarization-resolved detectors, and non-reciprocal optical elements. These devices may be more fault-tolerant than the computational elements described above; which is important as in the in the near term, devices built on monolayer 2D materials will have to contend with grain boundaries. Moving forward, however, understanding transport of valley information across grain boundaries will help inform if more complex valleytronic devices are possible on such polycrystalline material, or if single domain films are really required.

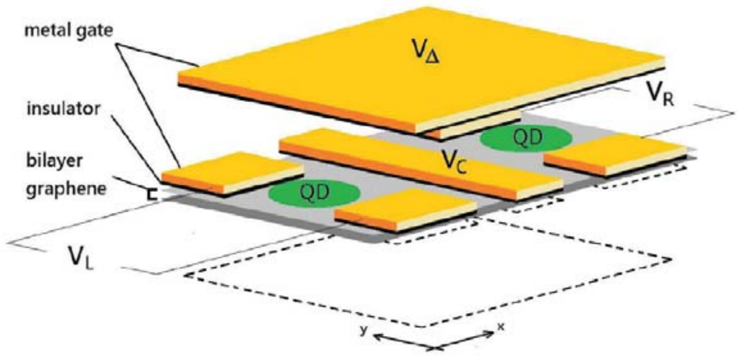

Figure 15: Proposed Valley qubit. From reference [40].

The above device concepts will reply upon certain basic building blocks. For example, transport of valley information will occur through an interconnect of some sort. This could be an optical interconnect which employs a high-fidelity transducer to convert valley information from the exciton, electron, or hole into a photon with the corresponding chirality. Or the exciton, electron, or hole could be used as an information carrier without converting the information into the optical domain. TMDs may not be the ideal material for long distance information transport, due to their low mobility. But this could be circumvented by using graphene interconnects if one can solve the problem of transferring valley information between the two materials. Perhaps this can be done through a clever device design which converts valley information into the spin domain, and back again. For some applications, elements to generate valley current gain is essential to allow cascading of devices.

All of these devices and building blocks rely upon the availability of scalable process technologies. For example, ohmic contact to TMDs is problematic. The choice of metal to use and protocols for deposition are not straightforward topics. It has been shown that inserting an hBN layer between the metal and the 2D material improves contact resistance, but it is not clear why. Developing recipes for TMD contacts which do not require heroic layer-transfer efforts would benefit researchers currently struggling with device measurements. It has also been suggested that gate-defined device boundaries edges produce better quality measurements than edges defined by lithography and TMD etching, but more work needs to be done on this topic. Simple electrical structures for monitoring the quality of device processing are extremely valuable. In addition to Hall bars and van der Pauw structures, more work needs to be done to reduce the experimental complexity of valleytronic property test structures. These include non-local Valley Hall Effect devices for valley diffusion and other combined electro-optic test structures for Kerr effect and electroluminescence measurements.

7. SUMMARY AND RECOMMENDATIONS

The Valleytronic Materials, Architectures, and Devices workshop was by all accounts a successful event which provided the first formal gathering of the nascent Valleytronics community. It is clear that the new physics associated with manipulation of the valley degree of freedom has the potential for transformative impact on information processing and other systems. Below we highlight some of the most salient points which came out of the meeting, including recommendations on the path forward.

7.1 SIGNIFICANT FINDINGS

Multiple degenerate minima in the conduction band of semiconductors are referred to as valleys, and devices which exploit that fact that electrons are present in one valley versus another are referred to as valleytronic devices. Practical realization of valleytronics requires that one can initialize, manipulate, transport and readout selectivity each valley state. Only hexagonal 2D materials such as graphene and transition metal dichalcogenides are able to meet this requirement at the present time; this is due to fundamental symmetries of the material. In particular, the isolation of monolayer MoS_2 in 2010 catalyzed an enormous response from the research community, as experimental observation of useful valleytronic effects first became possible.

Valleytronic applications can rely upon several different species as carriers of valley information: electrons or quasiparticles such as holes, excitons, or trions. There are tradeoffs between recombination lifetime, valley lifetime, valley coherence, and valley transport among these different species. In various TMDs, the valley lifetimes are 0.1 – 100 ps for excitons, 0.1 – 1 ns for trions, 1 – 100 ns for electrons, and up to 2 μs for holes. There is very little data on valley coherence time or valley mean free path.

Demonstrations of exciton valley coherence and of manipulation of the coherent state have just begun. Arbitrary rotations of a coherent state have not been demonstrated. It is not completely clear if valley coherence is even possible for electrons and holes.

It is essential to emphasize the deterministic growth of valleytronic-quality material as exfoliation from bulk crystals is not a viable route to practical valleytronic device fabrication. We define valleytronic-quality as possessing sufficient valley lifetime, valley coherence time, and valley mean free path to perform a useful function. All of the theoretical benefits of a valleytronic system are predicated upon the solid state physics of an ideal single crystal. Actual TMD growth results are far from ideal; although "large-area growth" is frequently reported, the material is far from the wafer-sized single crystal that one might envision. At a macroscopic scale the material is polycrystalline, non-continuous, with large regions of disorder. It will be impossible to produce practical valleytronic devices out of such material. It is not clear that heteroepitaxy of a monolayer material will ever be possible, yet growth of large scale, single crystal TMDs is essential for practical application of valleytronic devices.

Although there is a growing literature on observation of valley physics phenomena and on 2D material growth, there has been little critical analysis of practical valleytronics applications before this workshop. Some valleytronic device concepts have been proposed, including valley FETs, valley filters, and valley qubits. But we assert that there have been no valleytronic device concepts yet published which convincingly promise real-world performance advantage in practical systems. This is the most urgent technical challenge, as having a concrete application will catalyze research funding and focus research efforts.

7.2 ENGINEERING APPLICATIONS AND COMMUNITY INTEREST

Though it is commonly stated upon the discovery of a new material or physics phenomenon that it will enable new products and technologies, to achieve real-world impact the integrated device needs to provide significant performance or power advantages over the currently commercially available technology, and at similar cost. This is a formidable challenge, and we have attempted to be quite realistic in our assessment of the potential engineering impact of valleytronics. We have identified several areas in which the unique physics of valleytronic materials could meet this challenge.

1. A sub 60mV/decade switch as a supplement to or a replacement for silicon CMOS. The valley degree of freedom provides us with new ways of turning on and off valley currents, such as by tuning the phase relationship between K and K' electrons. This avoids the fundamental constraint of MOSFETs which are limited by the Fermi-Dirac distribution of electrons in the source.
2. A new quantum computing modality with advantages over superconducting qubits and trapped ion qubits. Advantages include scalability to large numbers of qubits, spin protection of the valley state (or valley protection of the spin state), optical addressability, and increased density. Other quantum applications such as sensing and communications can benefit from the ability to easily integrate TMDs with the extremely high density electronic and potentially photonic interconnections available on commercial microchips. This would enable true quantum technologies in portable mass-market applications like cell phones and wearables.
3. Non-reciprocal optics, specifically microphotonic optical isolators, polarization sensitive detectors for full-Stokes imaging, and chiral photon emitters for Quantum Key Distribution. Valleytronic materials provide the advantage that they are inherently chiral, and the chirality may be switchable. This would allow performance and/or power advantages compared to systems made of discrete macroscopic optical components.

We should emphasize that the strong light-matter coupling in monolayer TMDs allows a new way to access and manipulate quantum states, and that computation is but one application in which valleytronics can provide a practical method of exploiting quantum phenomena for practical use. For example, the most common form of quantum communication, Quantum Key Distribution (QKD), relies upon the generation of polarized photons, and the remote detection of that polarization state. Linear polarization and detection can of course be achieved with conventional discrete optical components. If these optical systems were scaled down to the microchip level, the societal benefit could be enormous, as one could provide secure quantum channels between everyday personal devices such as smart phones, tablets, and health monitoring devices. Valleytronics may be the most practical route to chip-scale integration of QKD, as the monolayer TMD materials naturally produce light of left- and right- circular polarization, and they can act as detectors of the same.

Another field which promises to exploit quantum phenomena for practical benefit is in the sensing of electric fields, magnetic fields, temperature, acceleration, rotation, time, and gravity. These are accomplished through the Zeeman or Stark splitting of electronic transitions in single atoms, atomic vapors, or solid-state defect centers, or by the interference of atom wavepackets as they traverse different paths in momentum space. These same quantum phenomena are available through the valleytronic manipulation of quantum states in TMDs. There has been little exploration of the possible benefit of valleytronic materials compared to atomic systems for sensing applications. This is an important topic to explore further, as the integration of monolayer TMDs directly on to a microchip may enable consumer products that would not be possible with the currently available quantum sensing technologies.

The development of quantum computing, sensing, and communication technologies may be more practical through the new methods of quantum state manipulation offered in valleytronic materials. As will all quantum technologies, there are still questions to be answered about coherence time, practical operation of the systems at elevated temperatures and in real-world environments, and integration with control electronics and other system elements. The design and engineering of valley-based quantum technologies would be well suited for inclusion in the National Science Foundation's Quantum Leap program, for example.

7.3 NEEDS AND CHALLENGES

One must not overestimate the maturity of valleytronic technology. It is also a harsh reality that for many applications (perhaps excluding quantum computing) near room temperature operation is a practical requirement. There are fundamental questions which need to be answered as well as technical challenges to be overcome.

1. Concrete device concepts. These device concepts must have the theoretical underpinnings to support real-world performance or power advantage over commercially-available technology. Specific devices of interest include: valleytronic logic gates, valleytronic memory elements, spintronic devices with enhanced performance through valley/spin injection or filtering, valley current switches, valley current filters, valley qubits, valley-preserving interconnects, and valley-current amplifiers.

2. Performing arbitrary rotations of the valley state around the Bloch sphere. Specific topics include: novel methods to break valley degeneracy, new ways to induce coherent superposition of states, performing rotations from K to K' not just around the equator, demonstrating and manipulating a coherent valley superposition of electrons, holes, or trions, developing valley analogs of NMR and spin echo, understanding the influence of spin-orbit coupling on valley coherence time and rotation of the valley state.

3. Improving valleytronic properties. The properties of interest include recombination lifetime, valley lifetime, and valley mean free path. How to mitigate the exciton exchange interaction, as well as understanding decoherence mechanisms (phonons, disorder, grain boundaries, point and extended defects, nuclear spins, etc.) for other species. Improving valley properties at room temperature. Exploring transfer of valley information between different materials, such as between MoS_2 and graphene.

4. Single crystal growth of valleytronic materials. Growth of large scale, single crystal TMDs by heteroepitaxy or homoepitaxy. Novel monolayer TMD growth methods such as from solution or by atomic layer sulfurization of metal films. Theoretical study of the thermodynamics and kinetic limitations of TMD domain size.

5. Understanding the structure-process-properties relationships of valleytronic materials. Exploring methods of healing defects to improve valleytronic properties. Understanding valley transport across grain boundaries. Substrates to enhance valleytronic properties. Improving the absolute efficiency and the selectivity of chiral light absorption and emission. Exploring the effect of alloys on valley properties. Designing materials with larger or smaller spin orbit coupling, or materials with significant spin orbit coupling in the conduction band. Investigating novel heterostructures such as oxides, nitrides and mixed phases.

6. Improved device processing. Develop easy-to-use techniques for preparing high quality, atomically sharp interfaces. Development of simple ohmic contacts to TMDs. Development of simple test structures to evaluate valleytronic material properties. Develop process technologies to reduce the observed variability in sample doping, and to intentionally control the doping level. Demonstrate a rudimentary integrated device, such as long distance transport of valley information by chiral photon emission, transport of that polarized photon through a waveguide, and back-conversion of the photon into an exciton in a different spatial location.

7.4 RECOMMENDATIONS

Valleytronics is no longer in the realm of obscure phenomena, we have just crossed a threshold where a critical mass of knowledge, researchers, and potential applications justifies a significant, coordinated investment in the field. The investment must be both significant and coordinated as the challenges to be overcome are great and they require interdisciplinary collaboration between researchers with distinct expertise, including theoretical solid-state physics, quantum transport measurements, ultrafast optical spectroscopy, novel device engineering, electronic device processing, computational materials science, and materials growth. We strongly recommend that funding agencies including NSF, SRC, and DARPA recognize the transformative potential of valleytronics technology and that a five-year multi-institutional program be established. The scope of the effort should at least match that of other recent national programs with similar goals, i.e., \$5-7 M/yr. Organizationally it could be a Center under the umbrella of a larger initiative, such as NRI or STARnet (now called JMP), or a stand-alone Center of Excellence similar to NSF's Center for Integrated Quantum Materials. The Center should not be dominated by a single institution; instead a call for proposals should be issued with performers applying to one of the six areas of critical need outlined above. To encourage multiple institution involvement and multi-disciplinary research, the topic would also ideally fit NSF's Emerging Frontiers in Research and Innovation (EFRI) which provides multiple awards on selected topics with funding at the level of \$2M per group of PIs. Research projects of this type address theory, experiments and device, component implementation which would be an ideal combination of studies necessary for advancing the field of valleytronics.

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