Metastable zero-field skyrmion lattice at room temperature in van der Waals $(Fe_{0.5}Co_{0.5})_5GeTe_2$

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Zero-field skyrmions at room temperature were discovered in a van der Waals 50% Co-doped Fe_5GeTe_2 (FCGT) with a high Curie temperature (T_c = 365 K) and novel non-centrosymmetric structure. [1] Here, we visualize the magnetic domains near room temperatures in FCGT thin flakes using a variable-temperature magnetic force microscope. The skyrmion lattice can be induced from stripe domains by a small external magnetic field and persists as a metastable state in zero field at room temperature. Interestingly, the skyrmion lattice gradually "melt" into the stripe domains with annealing temperature above 320 K. The metastable skyrmion lattice and its annealing behavior can be explained by a phenomenological picture of the free energy landscape. [2]

[1] H. Zhang et al., Phys. Rev. Mater. 6, 044403 (2022).

[2] H. Zhang et al., Sci. Adv., 8, eabm7103 (2022).

CMOS-back-end-of-line compatible AlScN/MoS_2 Ferroelectric Field Effect Transistors

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Abstract:

3D Monolithic integration of memory devices with logic transistors is a frontier challenge in computer hardware. This integration is essential for augmenting computational power concurrent with enhanced energy efficiency in big-data applications such as artificial intelligence. Despite decades of effort, there remains an urgent need for reliable, compact, fast, energy-efficient, and scalable memory devices. Ferroelectric Field Effect Transistors (FE-FETs) are a promising candidate, but requisite scalability and performance in a back-end-of-line (BEOL) process have proven challenging. Here, we present BEOL-compatible FE-FETs using two-dimensional (2D) MoS_2 channels and AlScN ferroelectric materials, all grown via wafer-scalable processes. A large array of FE-FETs with memory windows larger than 7.8 V, ON/OFF ratios of greater than 10^7, and ON current density greater than 250 μA/um, all at ~80 nm channel lengths are demonstrated. The FE-FETs show stable retention up to 10 years by extension, and endurance up to > 10^4 cycles in addition to 4-bit pulse programmable memory features, thereby opening a path towards 3D hetero-integration of 2D semiconductor memory with Si CMOS logic.

Spin-polarized scanning tunneling microscopy study of rare-earth monopnictide NdSb

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Rare-earth monopnictides are a family of materials simultaneously displaying complex magnetism, strong electronic correlation and topological band structure. The recently discovered emergent arc-like surface states in this family have been attributed to the exotic multi-wave-vector antiferromagnetic order, yet the direct experimental evidence has been elusive. Here we use spin-polarized scanning tunneling microscopy to investigate the magnetic order in NdSb. We observe the checkerboard magnetic contrast that is consistent with the non-collinear antiferromagnetic order with multiple modulations. Moreover, we discover a hidden magnetic transition of single to multiple modulations below the Neel temperature which coincides with the onset of the surface states splitting observed by angle-resolved photoemission spectroscopy measurements. The direct evidence of the non-collinear spin order in NdSb not only clarifies the mechanism of the emergent topological surface states, but also opens up a new paradigm of control and manipulation of band topology with magnetism.

Exciton Confinement in Atomically-Thin, Lateral Quantum Heterostructures

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Two-dimensional (2D) semiconductors are promising candidates for optoelectronic application and quantum information processes due to their inherent out-of-plane 2D confinement. In addition, they provide a platform to realize even low dimensional in-plane exciton confinement, for example, 0D quantum dots, for interesting optical and electronic properties. However, it remains challenging to realize such laterally confined 2D monolayer and control size-dependent optical properties systematically. Here, we demonstrate the observation of lateral exciton confinement in large-area 2D quantum heterostructures composed of $MoSe_2$ quantum dots inside a matrix of WSe_2 monolayer. We created the lateral heterostructures with an ultraclean interface using sequential epitaxial growth, and the size of triangular $MoSe_2$ quantum dots (15~60 nm) could be controlled with a short reaction time. Optical spectroscopies revealed the size-dependent exciton confinement in the $MoSe_2$ monolayer quantum dots, which also showed quantum emission on 10 nm-sized quantum dots in the cryogenic condition. Our study will be applied to developing in-plane quantum-confined devices in 2D materials for potential applications in quantum information.

Bulk Synthesis of Layered Van der Waals Materials at 2DCC

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Abstract: Layered van der Waals (vdW) materials have attracted significant attention due to their wide range of technologically relevant functional properties. Since they are able to be exfoliated to 2D atomic layers, they offer rich opportunities to seek new functional properties induced by quantum confinement. 2D materials as well as various heterostructures composed of 2D materials have been among central topics of contemproratory condensed matter physics and materials science. The 2DCC bulk growth team has been growing a wide range of vdW materials. One recent focus is synthesis of intrinsic magnetic topological insulators $MnBi_{2n}Te_{3n+1}$, including $MnBi_2Te_4$ (n = 1), $MnBi_4Te_7$ (n = 2) and $MnBi_6Te_{10}$ (n = 3). Recent studies have shown the combination of magnetism and nontrivial band topology in this material family can lead to a rich variety of topological quantum states such as quantum anomalous Hall insulators, axion insulators and an ideal Weyl semimetal state. We have not only synthesized both antiferromagnetic (AFM) and ferromagnetic (FM) phases for these compostions via Sb substitution for Bi or controlling crystal defects, but also found their carrier type and concentration can be tuned by the Sb content. In addition, we have also grown many other magnetic vdW materials, including AFM CrSBr (T_N = 132 K), $MnPS_3$ (T_N = 78 K), NdTe3 (T_N = 3 K), and FM CrI_3 (T_c = 61 K), $VAgP_2Se_6$ (T_c = 19K), NiI_2 (T_c = 60 K), $Cr_2Ge_2Te_6$ (T_c = 61 K), $CrTe_2$ (T_c= 310 K), etc.

Effect of pre-anneal chemistry on the growth and properties of epitaxial MoS_2 on sapphire

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One major unsolved question in the epitaxial growth of transition metal dichalcogenides on sapphire is the effect of surface chemistry. Prior studies have suggested that chalcogen atoms help passivate dangling bonds on the sapphire surface, thus enabling quasi- van der Waals epitaxy [1,2]. However, the exact impact of chalcogen passivation on the growth on TMD films is not well-understood, with the published literature being contradictory. In this work, we studied the effect of pre-annealing c-plane sapphire under H_2 vs a mixture of H_2 and H_2S, on the nucleation, growth, and properties of MOCVD-grown epitaxial MoS_2. When pre-annealed under pure H_2, the MoS_2 nucleates rapidly and randomly on the sapphire, quickly reaching saturation. These domains then laterally grow outwards, merging to form a coalesced film. In contrast, when the sapphire is pre-treated with a mixture of H_2 and H_2S, the MoS_2 preferentially nucleates along the sapphire step edges, likely due to preferential sulfur passivation of dangling bonds on the sapphire terraces versus steps. Due to the greater separation between the MoS_2 domains across a step terrace than between those along the same step edge, the MoS_2 forms a ribbon-like structure aligned with the steps. The resultant elongated grains were observed in coalesced films via scanning electron microscopy and transmission electron microscopy. Moreover, the orientation of holes and bilayers in H_2/H_2S pre-annealed films is rotated by 30° when compared to H_2 pre-annealed films, indicating a change in the epitaxial orientation. Furthermore, the holes in the H_2/H_2S pre-annealed films are locally well-aligned, indicating that growth is locally unidirectional, with the orientation changing depending on the terrace.

Coalesced films were grown after different pre-anneal conditions and characterized to determine the effect of the pre-anneal on the final film properties. The positions of the MoS_2 $(11\bar{2}0)$ peak obtained by in-plane X-ray diffraction (XRD) measurements show that the film grown on H_2 pre-annealed sapphire has greater compressive strain than when the film grown on H_2/H_2S pre-anneal substrates. Additionally, the H_2 pre-annealed sample displayed a $[11\bar{2}0]$ $MoS_{2(0001)}$ // $[11\bar{2}0]$ a-$Al_2O_{3(0001)}$ epitaxial relationship, while the epitaxy for the H_2/H_2S pre-annealed sample is rotated by 30° to $[11\bar{2}0]$ $MoS_{2(0001)}$ // $[1\bar{1}00]$ a-$Al_2O_{3(0001)}$. The peak positions for the E_{2g} and A_{1g} Raman modes were more uniform for the H_2/H_2S sample, indicating that it had more homogeneous strain. Additionally, the lower average E_{2g} mode center and lower photoluminescence (PL) peak position for the for the H_2/H_2S sample indicates that it had less compressive strain, matching the XRD results.

[1] Lin YC et al. Realizing Large-Scale, Electronic-Grade Two-Dimensional Semiconductors. ACS Nano. 2018;12(2): 965–975
[2] Xiang Y et al. Monolayer MoS2 on sapphire: an azimuthal reflection high-energy electron diffraction Perspective. 2D Mater. 2021; 8(2): 025003.

Fabrication and Characterization of Local Aluminum Bottom Gated Graphene Transistor with ALD Al2O3 Gate Dielectric

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In this work, a new method of incorporating an Al_2O_3 atomic layer deposited (ALD) gate dielectric material to a graphene field-effect transistor fabrication is introduced. This process uses aluminum as a local bottom gate electrode with 15 nm of ALD Al_2O_3 as gate dielectric, with PECVD TEOS serving as an etch stop to solve the dry-etch selectivity between the two materials. . Dirac points around 5 V has been achieved with metal-to-graphene contact resistance of ~1.8 kOhm-µm, and hole mobility of approximately 500 cm^2/Vs. In addition, a post-process polymer treatment with polyethyleneimine (PEI) results in a self-adjusted Dirac point variability based on self-electrostatic doping that can be exploited for various applications. The results demonstrate the feasibility of incorporating ALD-based Al_2O_3 on aluminum gate and has opened great potential and avenues to a more diverse device structure for graphene related field-effect transistors.

Transport studies on 2D ferromagnetic $Mn(Bi,Sb)_6Te_{10}$/BN/graphite tunneling junction and 2D antiferromagnetic $MnPS_3$/graphene QH heterostructures

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Two-dimensional van der Waals magnets hosting novel quantum states are fundamentally interesting and potentially useful in low-power electronics. In this poster, we report on the studies of ferromagnetic $Mn(Bi,Sb)_6Te_{10}$ using tunneling spectroscopy and magnon transport in antiferromagnetic $MnPS_3$ using non-local transport techniques. Transport measurements of exfoliated $Mn(Bi_{0.88},Sb_{0.12})_6Te_{10}$ sheets show a Curie temperature of ~11 K and a coercive field of ~ 0.02 T at 2 K, in agreement with bulk measurements. We build vertical tunnel junctions using graphite electrode and thin h-BN barrier to probe the surface density of states of $Mn(Bi_{0.88},Sb_{0.12})_6Te_{10}$ and observed a suppressed differential tunneling conductance in a small range of biases (~15 mV) near V_{dc}=0 at low temperatures. This observation is consistent with a magnetic exchange gap. We developed a new non-local transport method to study magnon transmission through $MnPS_3$, which utilizes the quantum Hall edge states of bilayer graphene as injector and detector. We study both linear response and thermally generated magnons systematically as a function of temperature and magnetic field and relate the findings to the magnetic properties of $MnPS_3$. This method can potentially be used to probe the magnetic order and excitations of other van der Waals magnets.

Photon Upconversion in a 2D Inorganic–Organic Semiconductor Heterostructure

AR. Dziobek-Garrett, C.J. Imperiale, M.W.B. Wilson, T.J. Kempa

Van der Waals heterostructures (vdWHs) comprised of stacked 2D crystal monolayers can be used to elicit emergent electronic and photonic phenomena. Moreover, energy transfer processes may be engineered via vdWHs by taking advantage of the atomically-abrupt, Å-scale, and topologically tailorable interfaces within them. Here, we prepare heterostructures comprised of 2D WSe_2 monolayers interfaced with DBP-doped rubrene, an organic semiconductor capable of triplet fusion. We fabricate these films over large areas entirely through vapor deposition methods, thereby demonstrating a pathway toward device-scale heterostructures. Time-resolved and steady-state photoluminescence measurements reveal both quenching of WSe_2 emission by rubrene and emission from the DBP species at 612 nm, for excitation at 730 nm, which is clear evidence of photon upconversion. Through an analysis of the decay dynamics in the heterostructure we conclude that excitation transfer from WSe_2 to the triplet state of rubrene proceeds on sub-nanosecond timescales. The dependence of the upconversion emission on excitation intensity is consistent with a triplet fusion mechanism, and we achieve maximum efficiency (linear regime) of the upconversion emission at threshold intensities as low as 110 mW/cm^2, which is comparable to the solar irradiance. This study highlights the potential for advanced optoelectronic applications employing vdWHs which leverage strongly-bound excitons in monolayer TMDs and organic semiconductors.

Critical Examination of Cross Quantum Capacitance on Electric Double Layer Gated 2D Field Effect Transistors

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2D semiconductor materials have been a focus of study for applications in next generation electronic devices due to their unique properties including high electrical and thermal conductivity [1]. These properties along with their unique band structures enable novel physics and applications including semiconducting to metallic (and even to superconducting) phase transitions [2]. To achieve such transitions, an ultrahigh local electric field and capacitance is required. Electric double layer (EDL) gating is a technique that uses ions in an electrolyte to control charge transport in an electronic material by field-effect, and has been demonstrated to induce high local electric fields (>1V/nm) and capacitance density (>1uF/cm^2) on a variety of 2D crystals [3]. In addition to geometric capacitance, quantum capacitance, related to the chemical potential of charge carriers in the semiconducting material, has acted as a parasitic capacitance that limits the total capacitance and carrier concentration. Recent investigations have revealed that quantum capacitance alone does not fully account for the loss of capacitance in experimental measurements. An additional cross quantum capacitance (CQC) has been proposed [4, 5, 6]. The CQC considers coulombic interactions between charges on the same "plate" of the capacitor and those of the opposing plate. Such interactions become significant only when the distance between the two plates of capacitor is sufficiently small, which is the case for EDL formed between ion conductor and monolayer 2D crystal. While some experimental studies have attributed the lower measured conductivity to CQC [5], none of them analyzed the experimental data based on CQC equations to prove or quantify the impact of CQC. In this study we conducted a critical examination of the theory of CQC [6], and our findings suggest that only under specific conditions would CQC decrease the total capacitance. We evaluate the conditions in which it may present itself and whether/how these conditions are physically realizable, these findings may help suggest device parameters to maximize the total achievable capacitance in EDL gated 2D crystal FETs.

1. Chhowalla, Manish, Debdeep Jena, and Hua Zhang. "Two-dimensional semiconductors for transistors." Nature Reviews Materials 1.11 (2016): 1-15.
2. Li, Wenbin, Xiaofeng Qian, and Ju Li. "Phase transitions in 2D materials." Nature Reviews Materials 6.9 (2021): 829-846.
3. Xu, Ke, and Susan K. Fullerton-Shirey. "Electric-double-layer-gated transistors based on two-dimensional crystals: recent approaches and advances." Journal of Physics: Materials 3.3 (2020): 032001.
4. Zhang, Haijing, et al. "Band filling and cross quantum capacitance in ion-gated semiconducting transition metal dichalcogenide monolayers." Nano letters 19.12 (2019): 8836-8845.
5. Piatti, Erik, Alberto Pasquarelli, and Renato S. Gonnelli. "Orientation-dependent electric transport and band filling in hole co-doped epitaxial diamond films." Applied Surface Science 528 (2020): 146795.
6. Berthod, Christophe, et al. "Theory of cross quantum capacitance." Physical Review Research 3.4 (2021): 043036.

Authors: Nader Sawtarie, Chengye Dong, Tim Bowen and Josh Robinson

Title: Defect engineering of graphene with plasma treatment for 2D metal confinement heteroepitaxy (CHet)

Abstract: Confinement heteroepitaxy (CHet) of 2D metals is a groundbreaking new technique for wafer-scale synthesis of air stable 2D metals. The first step in the CHet process is to thermally grow epitaxial graphene on a silicon carbide (SiC) substrate. Subsequently, defects are generated in graphene with plasma treatment to allow for the penetration of gaseous metal species though graphene and have access to the SiC substrate. Because it is thermodynamically favorable for the metal species to create covalent bonds with SiC, a thin (1-3 layer) film of 2D metal is formed between SiC and graphene. Originally, a high O_2 plasma treatment was used to ensure sufficient defect generation in graphene. However, the plasma treated graphene was heavily defective which could cause irreversible damage. Here, we show that by using helium as the plasma gas (with possible residual O_2 in the plasma chamber) a “gentler” plasma treatment process was created, and defects in graphene could be gradually generated by varying time of treatment (as shown with a monotonic increase in the defect “D” peak in graphene Raman spectra). Moreover, a minimum defect density of graphene for CHet was found which resulted in improved surface morphology of the graphene top layer after the CHet process (reduction in “worm” structure formation), opening the door for heterostructure formation with 2D metals. Furthermore, He plasma treatment has potential use for defect generation in the top protective graphene layer post-CHet for catalysis applications, an intriguing platform for 2D metals.

Dynamics of Photoluminescence Changes in Two Dimensional Dichalcogenides Materials

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Expanding the applications of 2D dichalcogenide materials requires a more thorough fundamental understanding. Specifically, the underlying cause of changes in the photoluminescent behavior of MoS_2 WS_2, and WSe_2 from laser elucidation are currently disputed. Slow and fast dynamics have been attributed to a variety of sources including oxygen passivation, surface contaminant removal, substrate interaction, and heating. Here, the time series progression of as grown MoS_2,WS_2, and WSe_2 photoluminescence spectra on sapphire will be presented.

Star-shaped WS_2 Monolayers with Twin Grain Boundaries Promoted by Molybdenum Atoms

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Monolayers of transition-metal dichalcogenides (TMDs) exhibit fascinating properties that make them attractive in optics, electronics[a], spintronics, and valleytronics[b], and it is of vital importance to understand and control their morphology to tune their physical properties[c]. However, the origin of their morphology evolution is still highly elusive, which hinders the synthesis of desired morphologies for specific applications. Herein, we report the controllable synthesis and formation mechanism of star-shaped WS_2 monolayers by artificially adding trace concentrations of molybdenum using a liquid-phase precursor-assisted approach. Fluorescence imaging and photoluminescence (PL) mapping of six-arm stars revealed bright lines between adjacent arms. To correlate the morphology and optical properties with the microstructure, dark-field transmission electron microscopy (DF-TEM) was implemented to confirm the presence of polycrystal domains with a 60° lattice misorientation and a mirror twin grain boundary. Detailed analysis of the grain boundary and molybdenum atom distribution was assessed using high-resolution, high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The relationship of the growth morphology of WS_2 stars and the molybdenum to tungsten ratio of the precursor was also carefully investigated. In corroboration with the experimental results, we further developed a multiscale model which combines density functional theory and the Wulff construction, for the observed morphology evolution of $WMoS_2$ domains as a function of local chemical environment during growth. Our study provides further insights into controlling the morphology of crystalline TMD monolayers.

References

(a) Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N., & Strano, M. S. (2012). *Nature nanotechnology*, *7*(11), 699-712.
(b) Tong, W. Y., Gong, S. J., Wan, X., & Duan, C. G. (2016). *Nature communications*, *7*(1), 1-7.
(c) Dong, J., Liu, Y., & Ding, F. (2022). *NPJ Computational Materials*, *8*(1), 1-11.

Graphene and Beyond: From Atoms to Applications Workshop May18-19, 2023

Abstract

Emergent moiré phonons due to zone folding in WSe_2-WS_2 van der Waals heterostructures

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Bilayers of 2D materials offer opportunities for creating devices with tunable electronic, optical, and mechanical properties. In van der Waals heterostructures (vdWHs) where the constituent monolayers have different lattice constants, a moiré superlattice forms with a length scale larger than the lattice constant of either constituent material regardless of twist angle. Here, we report the appearance of moiré Raman modes from nearly aligned WSe_2-WS_2 vdWHs in the range of 240 cm^{-1}-260 cm^{-1}, which are absent in both monolayers and homobilayers of WSe_2 and WS_2 and in largely misaligned WSe_2-WS_2 vdWHs. Using first-principles calculations and geometric arguments we show that these moiré Raman modes are a consequence of the large moiré length scale which results in zone-folded phonon modes that are Raman active. These modes are sensitive to changes in twist angle, but notably, they occur at identical frequencies for a given small twist angle away from either the 0-degree or 60-degree aligned heterostructure. Our measurements also show a strong Raman intensity modulation in the frequency range of interest, with near 0 and near 60-degree vdWHs exhibiting a markedly different dependence on excitation energy. In near 0-degree aligned WSe_2-WS_2 vdWHs, a nearly complete suppression of both the moiré modes and the WSe_2 A_{1g} Raman mode (~250 cm^{-1}) is observed when exciting with 532 nm CW laser at room temperature. Temperature-dependent reflectance contrast measurements demonstrate the significant Raman intensity modulation arises from resonant Raman effects.

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Electronic properties of 2D dimensional systems based on graphene and beyond

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Currently, two-dimensional (2D) atomic-layer-based materials are widely studied due to their unique electronic properties. One example is graphene [1], which has exceptional properties such as high carrier mobility, thermal conductivity, and optical transmittance [2]. However, graphene is semiconductor gapless, limiting its possible application in microelectronics. Thus, several searches for physical and chemical modifications of graphene to tune its electronic properties stimulated the study of new allotropic forms of carbon with sp2, sp-sp2, or sp2-sp3 hybridizations. Recently, a new 2D carbon allotrope family of sp2 and sp3 hybridized carbon has been proposed. It was reported that this so-called penta-graphene structure, composed of pentagonal rings, is likely to exist as the absence of imaginary modes in its phonons band structure indicates dynamical stability [3]. In another proposal, Ram et al. demonstrated the strength and electronic properties of a new wide gap semiconductor carbon allotrope formed by combinations of sp2 and sp3 hybridized carbon but composed of 4 - 6 carbon rings, the so-called tetrahexcarbon structure [4]. In this study, we propose a new family of quasi-2D carbon nanostructures with mixed sp2-sp3 hybridization, called tetragraphene, where tetrahexcarbon structure is a representative example of this family [5]. In the addiction, we got the electronic properties of another class of materials 2D dimensional, the transition metal dichalcogenides (TMDCs). This class of systems showed unique electronic, optical, and surface chemical properties [6], making the TMDCs attractive in diverse applications [7]. In this work, we investigated how vacancies in two-dimensional MoSe2, “defect engineering,” had addiction states near the Fermi level. All the physics proprieties were obtained using quantum-based computational methods by first-principles calculations within the framework of DFT as implemented in the SIESTA code [8].

[1] K. S. Novoselov, A. K. Geim, et. al. Science **306**, 666-669 (2004);

[2] D. S. L. Abergel, V. Apalkov, et. al. Adv. Phys. **59**, 261-482 (2010);

[3] S. Zhang, J. Zhou, Q. Wang, X. Chen, Y. Kawazoe, P. Jena. PNAS **8,** 2372 (2015);

[4] B. Ram and H. Mizuseki. Carbon **137**, 266 (2018);

[5] F. M. de Vasconcelos, A. G. S. Filho, V. Meunier and E. C. Girão. Carbon **167,** 403-413 (2020);

[6] M. Chhowalla, H. Zhang, et. al. Nat. Chem. **5**, 263–275 (2013);

[7] X. Chen, C. Liu, S. Mao. Nano-Micro Lett **12**, 95 (2020);

[8] A. García, N. Papior, A. Akhtar, et. al. J. Chem. Phys. 152, 204108 (2020).

Topochemical manipulations on ternary layered borides toward the synthesis of two-dimensional materials

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Abstract: Top-down synthesis is a robust method for achieving novel two-dimensional materials dating back to the scotch tape method of graphene synthesis in 2004. Over the last ten years, this approach has expanded beyond Van der Waals materials and into the topochemical manipulation of bulk layered materials. MAX phases, where M is a transition metal, A is an interleaving metal or metalloid, and X is carbon or nitrogen, are the most well-studied of these bulk materials. This is due to the anisotropy in bond strength between the layers where the M-X elements have strong covalent bonding and the M-A bonds are metallic in nature, allowing for the A element to be selectively removed. Once the A element is removed, the M-X layers can be exfoliated resulting in a MXene. The A element is most commonly removed with HF which is hazardous and requires the M-X layers to be very robust. Certain MAX phases cannot withstand HF, and neither can the MAB phases, which are the boride analog of MAX phases. If we want to continue to synthesize new two-dimensional materials from these bulk layered precursors, we must find a gentler way to remove the A element.

There have been a few successful attempts to remove the A element from MAX phases without fluorine present, most notably with the use of molten salt. When the MAX phase Ti_3AlC_2 is mixed with excess $ZnCl_2$ and heated at 550 °C for 5 hours the aluminum layer is selectively removed through redox chemistry, resulting in a MXene. When we tried this method on the MAB phase MoAlB, however, we saw only partial removal of the aluminum and progression toward the metastable material Mo_2AlB_2. Upon running the reaction for 170 hours we synthesized phase pure Mo_2AlB_2 with no evidence of two-dimensional material formation. This difference in reactivity between MAX and MAB phases provides insights into the importance of stoichiometry, bond strength, and bond anisotropy. We also gained understanding of the reaction pathway by performing the reaction with various metal chloride salts which revealed that redox chemistry between the metal species is not solely responsible for the progression of this reaction. This comparative study helps us to better understand why some bulk ternary compounds are easier to etch than others and begins to lay out the requirements necessary for etching MAB and fragile MAX phases.

Field-Controlled Ion-Locked Polymorphic Electronics for Hardware Security

D.D. Sarawate, P.M. Prem, K. Xu, E.J. Beckman, and S.K. Fullerton-Shirey

Hardware security comes at a high price in the U.S. at $200 billion annually. Polymorphic electronics provide a potential solution to hardware security threats by preventing unauthorized parties from accessing circuitry information through reverse engineering. The goal of this work is to obscure a device's function by taking advantage of electric double layer (EDL) gating to reconfigure NAND and NOR gates on-demand. The key innovation is a custom synthesized polymer electrolyte that reacts under an electric field created by the EDL (~V/nm) and locks the ions in the EDL into place by crosslinking the polymer electrolyte. Specifically, the electric field aligns the dipoles of the electrolyte into more favorable reaction orientations which will initiate chemical crosslinking reactions. We synthesized a custom electrolyte called poly(2-(diethylamino)ethyl methacrylate-co-poly(ethylene glycol) methyl ether methacrylate) (P(DEAEMA-co-PEGMA)) in varying DEAEMA:PEGMA molar ratios of 1:2, 2:1, 1:1. To this, $LiClO_4$ is added in a 20:1 molar ratio of polymer to salt. The crosslinker, dibromohexane (DBH) is added in a 1:2 molar ratio of DBH:DEAEMA. Ion mobility is confirmed in a lateral, parallel-plate capacitor geometry, and graphene field effect transistors (GFETs) are used to test locking. Preliminary evidence of ion locking was observed by programming GFETs at positive gate voltages ($V_G > +2$ V), and then sensing the doping shift and ON/OFF ratio via transfer measurements. Positive programming voltages less than +2 V showed no effect on the doping; however, the device becomes more n-type as V_G is increased from +2 to +5 V. For a non-locking electrolyte, grounding the gate will dissipate the EDL and reverse the doping effect. In the case of the locking electrolyte, the doping effect persisted even after the gate bias is grounded indicating ion locking at the graphene surface. This process was followed by application of negative V_G to demonstrate a semi-permanent—but reversible—doping effect. As V_G is increased from -1 to -5 V, the Dirac point shifts back towards original position, suggesting that the doping effect is reversible, but non-volatile. The next step is to quantify the doping effect by measuring sheet carrier density before and after locking using Hall measurements. Chemical characterization of the polymer electrolyte, including identifying functional groups with NMR and measuring molecular weight are ongoing.

High-resolution S/TEM Imaging and Cathodoluminescence of 2D TMD Heterostructures

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Two-dimensional (2D) transition metal dichalcogenides (TMDs) are technologically consequential materials owing to their attractive properties such as indirect to direct band gap transition upon thinning to a monolayer [1]. Integration of multiple 2D TMDs into heterostructures in various geometries (vertical and in-plane) has accelerated the development of these materials into targeted applications in optoelectronics [2]. However, the electronic and optical performance of these heterostructures is highly dependent on the interfaces formed between constituent TMDs [3]. For example, defects and strain at the interface, originating from the lattice mismatch between the two 2D materials, can significantly affect the interface structure and consequently the heterostructure performance [4]. At the same time, this provides an opportunity to control the interface characteristics by careful selection of TMDs and synthesis methods to tune the properties of resulting heterostructures. We employ scanning/transmission electron microscopy (S/TEM) imaging as well as cathodoluminescence (CL) and Electron Energy Loss Spectroscopy (EELS) spectroscopy to investigate the interface atomic structure, defects, epitaxy, and strain between various TMD 2D crystals in vertical and in-plane heterostructure. This work explores vdW epitaxy in vertical heterostructures as well as optical response of the quantum dots in in-plane 2D heterostructures.

[1] Splendiani, A. et al., Nano Lett. **10**, 1271–1275 (2010).
[2] Geim, A. K. & Grigorieva, I. V., Nature **499**, 419–425 (2013).
[3] Pant, A. et al., Nanoscale **8**, 3870–3887 (2016).
[4] Xie, S. et al., Science **359**, 1131–1136 (2018).
[5] This work was supported by the National Science Foundation (NSF),

Local Write, Read, and Erase of a Graphene/Monolayer Electrolyte/h-BN Heterostructure via Electric Force Microscopy

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A solid-state, non-volatile memory based on electric-double-layer (EDL) gating using a monolayer electrolyte (ME) has been developed in our lab. This ME comprises cobalt crown ether phthalocyanine (CoCrPc) and $LiClO_4$ that forms an ordered array on the two-dimensional (2D) crystal surface. Each crown ether can solvate one metal cation that is stable in two distinct states in the crown – one near the 2D crystal, creating a low-resistance state, and the other further away, creating a high-resistance state. The switching mechanism can be triggered by an electric field via a transistor architecture with a global back-gate. Here, we investigate a method to locally toggle the ions through the crown using an atomic-force microscopy (AFM) tip. In contrast to a three-terminal transistor, we use a two-terminal stack of graphene/ME/hexagonal boron-nitride (h-BN) on p-doped Si, prepared by dry flake transfer. P-doped Si acts as one terminal, and the AFM tip/graphene serves as the second. AFM is used in electric force microscopy (EFM) mode to simultaneously write/erase and read the stacks. The AFM tip contacts graphene as a charge source to inject charges locally while the p-doped Si is grounded. The ion locations are switched using a "write" voltage < -0.5 V, and the difference in electrostatic force between the tip and the written regions is detected using a non-contact "read" voltage of +2 V that does not disturb the ion position. The write voltages range from -0.5 to -6 V. The increasing negative write voltages can attract the Li^+ to the graphene surface, resulting in n-doping and increasing tip-sample at- traction when ions are closer. The surface charge density (σ) of the written region is calculated as it increases from $\sim 3 \times 10^{11}$ cm^{-2} to $\sim 6 \times 10^{12}$ cm^{-2}. After the write, a reverse "erase" bias is applied to the same region (from 0.5 to 6 V) to push the ions away from the graphene, and is read with the same sensing voltage. The σ decreases back to $\sim 1 \times 10^{11}$ cm^{-2}, indicating the reversal of the doping effect. Control samples ($\sigma \sim 10^{11}$ cm^{-2}) without the ME (i.e., graphene/h-BN) are measured using the same method to confirm the increasing σ is originated from ME. This work is supported by the NSF under Grant # NSF-DMR-EPM CAREER: 1847808.

Understanding rare earth point defects in MoS2 and WS2

Kang, H. and Muechler, L.

Rare earth point defect in 2D materials such as MoS2 and WS2 have recently attracted interest for use as single photon emitters. However, the defect chemistry of rare earth dopants is not well studied. In this poster, we investigate the formation energies and electronic properties of various types of point defects in these systems. We show that apart from the expected f-electron states in the gap, there are other states that originate from hybridization between host and rare earth states. We discuss the generality of the findings, particular the potential impact on the optical properties and the consequences for downfolding methods.

High Throughput Potential Neural Network Algorithm to Exploit Non-local Interactions on Graphene Interface

J.K. Averitt, J. Starobin, T. Ignatova

In this study, we investigated the molecular interactions of two distinct polymers with graphene. Specifically, we propose an algorithm which involves Energy Decomposition Analysis using a Force Field (EDA-FF) from Potential Neural Network (PNN) optimized geometry and high throughput screening. Our computational analysis revealed that the affinity of the two different polymers for graphene is primarily determined by the electrostatic interactions between the polymers.

Strain-induced semiconducting to semi-metallic phase transition in $MoTe_2$ using a single-ion conductor

Shubham S. Awate, Ke Xu, Jierui Liang, Benjamin Katz, Ryan Muzzio, Jyoti Katoch, Vincent H. Crespi and Susan Fullerton-Shirey

Commonly studied transition metal dichalcogenide (TMD) crystals exhibit polymorphism, where the electronic structure of the material changes significantly with a change in the crystal structure. MoTe2 has gained particular interest because the potential energy difference between the semiconducting 2H and semi-metallic 1T' phase is lowest (40 meV) among TMD polymorphs, making it promising for low voltage phase change memory and transistors. Although the 2H phase is the most stable form, it can be transformed to 1T' by 0.3 - 3% by tensile strain thereby causing a large change in the electronic conductivity. Recent studies have experimentally shown this phase transition by mechanically stretching the entire substrate or applying local mechanical strain using atomic force microscopy (AFM) tip, but both strain methods would be difficult to implement in CMOS. What is needed is a straining mechanism driven by field-effect, where a single device can be controlled electrically by a nearby gate.

Here, we employ an 'ionomer' or single-ion conductor to impart strain, which has been used by the polymer physics community for artificial muscles and actuators. An ionomer contains mobile cations but has anions that are covalently bonded to a polymer backbone. Under an applied electric field, the cations accumulate at the MoTe2 surface, effectively controlling electron transport in the material, while anions maintain their position in the polymer backbone creating a charge imbalance. The imbalance causes the ionomer to bend, which then induces strain in the MoTe2.

In this work, the electrical and structural properties of a suspended MoTe2 FET are measured simultaneously using a home-built set-up combining electrical measurements with Raman spectroscopy. With no gate voltage (V_G) applied, the insulating 2H phase is confirmed. For $V_G > 2.5$ V, the 1T' phase is detected by a significant decrease in the electrical resistance accompanied by a characteristic 1T' peak in the Raman spectra. However, because a large portion of the flake is supported and not suspended, a contribution from the 2H phase persists. Mapping the 2H and 1T' peaks across the entire flake reveals that the phase transition is reversible (i.e., the flake reverts to the semiconducting 2H phase when the voltage is removed), which is an essential feature of a memory and a switch. The output characteristic of the FET shows large change in the

I_D-V_G slope for V_G >1.5 V. Further, metallic conduction is confirmed by positive temperature coefficient of resistance for V_G = +2 and +3 V. Lastly, time-dependent Raman spectroscopy is performed to study the phase change dynamics. These proof-of-concept results are encouraging because there is plenty of opportunities to optimize the device structure and the ionomer to engineer a complete transition and enable a true low voltage phase change memory and transistors.

Behavior of Excited States in 2H and 3R Bilayer WSe_2

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Transition metal dichalcogenide bilayers exhibit improved stability and higher carrier mobility compared to their monolayer counterparts, and may be attractive for a variety of applications. Both 2H and 3R bilayers are energetically stable and are expected to exhibit semiconducting behavior. However, 2H has received the bulk of attention due to its ready availability in the form of mechanically exfoliated flakes. Here, we detail the energies and temperature dependent behaviors of the ground and the first excited excitonic states in both 2H and 3R WSe_2 bilayers. Samples are obtained through chemical vapor deposition, encapsulated with hBN, and reflectance contrast (RC) is measured to identify 1s and 2s excitonic states. At cryogenic temperatures, a splitting of approximately 17 meV is experimentally observed in both the 1s and 2s states of 3R bilayers. This splitting is consistent with our DFT calculations and is due to lack of inversion symmetry, with the two peaks corresponding to distinct excitonic transitions in the upper and lower layers of the 3R WSe_2. As temperatures increases, excitonic states broaden and RC intensity decreases, preventing detection of 2s states above 100 K. The 1s state is evident at all temperatures between 4 K and 300 K, and splitting of the 1s state in 3R samples is detectable to approximately 250 K. This work provides much needed insight into bilayer systems and demonstrates that interlayer interactions are strong enough to significantly modify the optical properties in WSe_2 samples.

Visualizing Temperature Driven Ferromagnetic to Antiferromagnetic Transition in MnSb2Te4

Wenbo Ge (Rutgers), Weida Wu (Rutgers), Jiaqiang Yan (ORNL)

The intrinsic magnetic topological insulator MnBi2Te4 exhibits rich exotic quantum phenomena[1,2]. However, the theoretically predicted Dirac mass gap is susceptible to native magnetic defects, which often leads to conducting bulk state[3]. Therefore, understanding the role of magnetic defects is essential in engineering topological materials. The same type of magnetic defects in the isostructural compound MnSb2Te4 show higher concentration and tunability, making MnSb2Te4 an ideal platform to investigate the interplay among magnetic defects, topological band structure and magnetism. It has been reported that by tuning the Mn/Sb site mixing, ferromagnetic (FM) order can be introduced into MnSb2Te4 and compete with the antiferromagnetic order[4]. Magnetic imaging of ferromagnetic domains in some site mixing engineered MnSb2Te4 systems has been reported in our previous work[5]. In this work, we directly visualize the temperature driven FM-AFM phase transition with TC=24K and TN=15K in single crystals of MnSb2Te4 using cryogenic Magnetic Force Microscopy. Our work reveals the complex magnetic competition in MnSb2Te4 and paves the way for understanding the role of magnetic defect in the magnetism of MnSb2Te4.

1. Liu *et al. Nature Materials*, 19, 522–527 (2020).
2. Deng *et al. Science* 367, 895–900 (2020).
3. Liu *et al. PNAS* 2022 Vol.119 No.42 e2207681119.
4. Liu et al. *Phys. Rev. X* 11, 021033.
5. Ge *et al. Phys. Rev. B* 103, 134403.

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Physical Vapor Deposition Techniques of Metals on 1L MoS_2

A. D. Agyapong, M. S. Rahman, C. Chen, N. Trainor, J. M. Redwing, and S. E. Mohney

The two-dimensional transition metal dichalcogenide (TMD) molybdenum disulfide (MoS_2) has desirable properties for use as a channel material in nanoscale field-effect transistors (FETs). However, contact resistance at the metal/semiconductor interface can hinder FET performance. Recently, lower contact resistances have been achieved and ascribed to factors such as the use of semimetal contacts or the preparation of "clean" contacts. Here we examine the impact of the metal deposition technique on MoS_2 monolayers through Raman spectroscopy with backside illumination. This approach is a fast and non-destructive way to observe changes at the buried metal/1L MoS_2 interface. We compared e-beam evaporated and sputtered metal films on 1L MoS_2, which provide insights into both damage and doping. We also note differences in Raman spectra after metallization depending on the original quality of the MoS_2, which is expected to be another factor in determining the contact resistance.

Characterization of Single Photon Emitters in Hexagonal Boron Nitride Nanoflakes

E. Dimitrov, G. Bepete, S. Ozdemir, M. Terrones

Single-photon emitters are an essential component in the emerging applications of quantum communication, quantum computing, and integrated quantum photonics. Hexagonal boron nitride is of particular interest as a 2D material with a wide bandgap, which allows it to host a wide range of visible to UV emitters and retain stability at room temperature. These emitters arise from spatially isolated defects which introduce mid-gap states which can be excited to act as emitting color centers. However, the specific nature of these defects in hBN is still not well understood, due to the difficulties in locating and probing single atom defects in multilayer materials.

In this work we investigate the properties of single photon emitters in hBN nanoflakes, which have been dispersed in solution the drop-cast onto a flat silicon substrate. These flakes are commercially available and have the advantage of being simple to prepare, stable, and host a wide range of emitters. To characterize these emitters, we perform photoluminescence mapping across the dispersed flakes to locate various emitters. Using a marked substrate, we can relocate these emitters at other times or under different systems for further characterization. Once located, a Hanbury-Brown-Twiss interference setup is used to acquire the photon antibunching statistics to demonstrate that an emission peak is the result of a single photon emitter. We have located multiple emitters in the range of 560-650nm with values as low as $G^2(0)<0.1$.

These emitters are stable in room temperature and under atmospheric conditions for multiple months and maintain stable emission across hours of direct excitation. The presence of multiple stable wavelengths suggests that a wide range of defects could be responsible for these emissions. In addition, high quality single photon emitters have been found in dispersed films created from chemically exfoliated hBN nanoflakes, which opens to possibility for alteration of the properties of these emitters through chemical treatments.

Computational simulations of Raman-spectroscopy-related properties of materials

*Natalya Sheremetyeva, Michael Lamparski, Mayada Fadel, and Vincent Meunier

Abstract: The field of two-dimensional layered materials (2DMs) continues to rapidly grow. Many properties of these novel materials depend on their structural features. Therefore, exact property control relies on the careful characterization of 2DMs. Raman spectroscopy is a nondestructive technique that can identify even small structural and electronic changes. The interpretation of experimental spectra can often be challenging. Computationally obtained Raman spectra based on first-principles theory have been shown to aid in precise characterization efforts. Here, we showcase a few studies carried out in our group on computational simulations of Raman spectra and related quantities using Density Functional Theory (DFT), as well as modern analysis approaches based on data science and machine learning.

Realizing Gate-All-Around Vertical Nanowire Field-Effect Transistors Based on Van Der Waals Epitaxial InAs-on-2D Heterostructures

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III-V semiconductors show promise as channel materials in next generation nanoelectronics.[1,2] Among III-V materials, InAs stands out as a potential replacement for n-type channel material in complimentary metal-oxide-semiconductor (CMOS) based devices.[3,4] Compared with silicon, InAs offers 30 times the electron mobility and a higher ON current, and when grown as a 1D InAs nanowire (NW), this mobility is further enhanced compared to thin-film and bulk InAs.[3] As such, NW FETs were developed to harness the potential of III-V materials, where a gate-all-around (GAA) geometry offers better electrostatic gating of NWs but proves to be a much more difficult fabrication process, especially with vertical NWs.[3] In order to solve this issue, electric double layer (EDL) gating can be used. EDL gating is a method which uses an electric field to control mobile ions within an electrolyte to create strong local electric fields. Due to the accumulation of ions in the electrolyte ~1 nm from the channel, fields on the order of 10 MV/cm can be achieved, allowing for high carrier density in semiconducting materials (including 2D and III-V materials)[5]. Additionally, the strength of EDL gating is weakly dependent on gate to channel distance, which allows for flexibility in device geometry without sacrificing carrier density. EDL gating can support otherwise difficult to fabricate geometries such as vertical GAA NW FETs. In this study, we will investigate the challenges that come with fabricating these novel devices, as well as electrical characterization. The device geometry consists of vertical InAs NW arrays epitaxially grown on graphene, with solid electrolyte permeating between NWs, topped with a metal electrode contacting the top of the NWs. Characterization on the uniformity and thickness of the electrolyte deposition will be performed via SEM and AFM. The impact of different deposition methods on the mechanical structure of NWs will also be discussed.

1. R, Ullah, et al, *Physical Review Materials* 2.2 (2018), 025601.
2. Barrigón, Enrique, et al, *Chemical Reviews* 119.15 (2019) , 9170-9220.
3. Zhang, Chen, et al, *IEEE Transactions on Electron Devices* 63.1 (2016), 223-234.
4. Lieb, Johanna , et al, *Advanced Functional Materials* 29.3 (2019), 1804378.
5. Xu, Ke and Fullerton, Susan, *J. Phys. Mater* 3.3 (2020) 032001.

Rational Design of Defects with Small Huang-Rhys Factors in 2D Materials

To serve as an ideal single-photon emitter, a point defect needs to satisfy a long list of criteria. One such criterion is producing indistinguishable photons, which requires a small electron-phonon coupling for the excited state involved, characterized by a small Huang-Rhys factor. Although Huang-Rhys factors can be numerically computed from first-principles, there lacks a rational design principle that can explain and identify defects with small Huang-Rhys factors. In addition, computing Huang-Rhys factors from first-principles is often a time-consuming and computationally challenging task – struggling with not only slow convergence issues with respect to supercell size, but also with finding excited-state solutions involving degenerate defect levels. For this reason, computing Huang-Rhys factors are usually applied to limited defect candidates at the end of aggressive screening procedures, missing potential hits.

Here we propose a rational design principle that targets small Huang-Rhys factors: an increased similarity in bonding/anti-bonding character between the excited and ground state of a defect is a strong indicator of a small Huang-Rhys factor. Establishing this principle would allow us to estimate Huang-Rhys factors from a single ground-state calculation. As prototypical examples, we demonstrate this principle for realistic single-photon emitter candidates in hBN such as boron and reconstructed nitrogen vacancies in. Huang-Rhys factors are first calculated from first-principles using the one-dimensional configuration coordinate approximation, as well as full calculations involving phonon spectra, where we carefully extrapolate towards the dilute defect limit. Calculated Huang-Rhys factors are then compared with the degree of bonding-character similarity between excited and ground states.

MBE growth of In-Se system for high-performance field effect transistor

L. Derrick Shao Heng, H. Maria, E.H. Roman, and M.R. Joan

Indium selenide has recently gained renewed interest in the two-dimensional (2D) material family due to its wide range of potential applications. Its ultra-thin form and back-end-of-line friendly synthesis parameters make indium selenide a promising candidate for high-performance field effect transistors. The monochalcogenide InSe has already demonstrated electron mobility of up to 1000 cm2/V·s at room temperature through exfoliation from a single crystal. However, large-scale production of InSe films still requires a time-consuming growth mapping process, regardless of the deposition technique. Molecular beam epitaxy (MBE) has the advantage of precise control over atomic flux, growth temperature, and deposition rate, making it ideal for growing high-quality crystalline InSe films. Nevertheless, growing a phase pure InSe film generally requires an extensive growth window mapping process due to the coexistence of multiple In-Se phases and Se's much higher volatility than In. Moreover, reported growth parameters are of limited significance in approaching the stabilization of a specific In-Se phase, which is a significant challenge for reproducibility in the field.

The sesqui-chalcogenide In_2Se_3 is predicted to be one of the suitable 2D ferroelectric materials for new memory devices. However, phase assignment and characterization are still controversial due to the numerous combinations of polymorphs (α, β, and γ) and polytypes of In_2Se_3. The phases are determined by the crystal structure of repeating quintuple layers, and the polytypes are determined by the stacking sequences of the quintuple layers. While existing reports suggest that each phase exhibits in-plane or out-of-plane polarization, many of these publications are incomplete and fail to identify the specific phase or polytype. Thus, a deeper understanding of all In_2Se_3 phases and polytypes is required, as ferroelectricity is coupled to the crystal structure. However, to date, there has been no systematic study exploring the synthesis and detailed structure of each phase and polytype and connecting the structures to their respective ferroelectric properties. It is also challenging to predict which phase and polytype will exhibit on a particular substrate.

In this poster, we present a strategic approach to systematically map out the growth window of InSe on Si(111) substrate by MBE. The film composition was measured by X-ray diffraction (XRD). We then characterized the surface morphology and growth mode of the resulting films using atomic force microscopy, as well as identified the InSe as γ phase through cross-section scanning transmission electron microscopy (STEM) imaging. Additionally, we demonstrate the growth of β-In_2Se_3 and γ-In_2Se_3 on sapphire and Si(111) by MBE, including the phase identification through XRD and Raman spectroscopy, polytype identification of β-In_2Se_3 with (STEM) atomic visualization, and initial polarization measurements. Our findings will pave the way for a more comprehensive understanding of InSe and In_2Se_3 materials and contribute to the development of high-performance field effect transistors.

Achieving a Linear Synaptic Update in Electric Double Layer Gated 2D Field Effect Transistors for Applications in Artificial Neural Networks

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In order to overcome the Von Neumann bottleneck and increase the power efficiency of modern computation, neuromorphic computing has emerged as a potential solution which allows for parallel computing, adaptive learning, and long-term potentiation for use in neural networks[3]. Electric double layer (EDL) transistors use ions to induce a high charge carrier density inside the channel, and both long and short term ionic response closely resembles a biological synapse. EDLTs based on 2D crystal allow for low power operation, making it a promising candidate for use in artificial neural networks[1,2]. In order for EDLs to be viable for this application a linear synaptic response is highly required (a proportional weight update in response to a voltage input)[5,6], however this has proven to be challenging with a constant input voltage for a given frequency. This study examines the reasons why we see a non-linear weight update, caused by the induced electric field between ions resulting in an exponential decay between input pulses, related to the concentration of the EDLs. This leads to an increasing rate of weight decay, which eventually stagnates the output signal resulting in no weight update over concentric pulses. This behavior was examined uses Finite Element Modeling within COMSOL using the modified Nernst-Poisson-Planck equations[7]. 10 pulses were given as input at 100Hz, and as expected the EDL concentration saturated within these 10 pulses at less than half of the maximum concentration possible with the same steady voltage. Next we were able to show that a linear EDL concentration was possible through a varying magnitude voltage (i.e nonlinear input). The challenge with this approach comes with the non-linear dissipation between pulses, making it necessary to predict the dissipation and required voltage. Based on the change in EDL concentration over time (dc/dt) we were able to create an empirical relationship between (dc/dt), concentration and input voltage which we were then able to couple with the COMSOL model to predict the necessary inputs in a single computation. For the 100Hz trial over 10 pulses a linear weight update with R^2 of 0.996 was achieved with a 13% increase is final EDL concentration with inputs ranging between 0.25-3V (within the electro-chemical window of PEO:$LiClO_4$) and still has potential to continue to increase, which was not possible with a constant input magnitude. These preliminary findings show possibilities for extending this behavior for use in artificial synapses and EDL based synaptic networks. Moving forward the group is focused on experimentally verifying the model parallel plate capacitor geometry and graphene-based EDL transistors.

1. Jiang, Jie, et al. *Nanoscale* 11.3 (2019): 1360-1369.
2. Xu, Ke, and Susan K. Fullerton-Shirey. *Journal of Physics: Materials* 3.3 (2020): 032001.
3. Schuman, Catherine D., et al. *arXiv:1705.06963* (2017).
4. Zhu, Jiadi, et al. *Advanced Materials* 30.21 (2018): 1800195.
5. Sung, Changhyuck, et al. *Nanotechnology* 29.11 (2018): 115203.
6. Jacobs-Gedrim, Robin B., et al. *2017 IEEE International Conference on Rebooting Computing (ICRC)*.
7. Lee, Seunghyeon, et al. *Biosensors and Bioelectronics* 170 (2020): 112620.

Optical Properties of Single-Layer WS2 and Substrate Influence

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Abstract: Among the most studied semiconducting transition metal dichalcogenides (TMDCs), WS2 showed several advantages in comparison to their counterparts, such as a higher quantum yield, which is an important feature for quantum emission and lasing purposes. We studied transferred monolayers of WS2 on a drilled Si3N4 substrate in order to have insights about on how such heterostructure behaves from the Raman and photoluminescence (PL) measurements point of view. Our experimental findings showed that the Si3N4 substrate influences the optical properties of single-layer WS2. Beyond that, seeking to shed light on the causes of the PL quenching observed experimentally, we developed density functional theory (DFT) based calculations to study the thermodynamic stability of the heterojunction through quantum molecular dynamics (QMD) simulations as well as the electronic alignment of the energy levels in both materials. Our analysis showed that along with strain, a charge transfer mechanism plays an important role for the PL decrease.

2D Layered Chalcogenides from Ordered Vacancy Compounds

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Abstract

Simultaneously predicting and explaining the formation of 2D layered materials via computational methods remains challenging. Current methods can only predict the crystal structure or classify between 2D and 3D yet offer little reasoning as to why they occur in the first place. We propose stabilization by vibrational entropy to rationalize stabilizing 2D structures. This is then generalized to ordered vacancy compounds – stoichiometric 3D bulk compounds with an ordered distribution of vacancies – which can be transformed into 2D layered structures by repositioning vacancies. This principle is applied to several compounds with competing 2D/3D phases and the unique case of quasi-2D morphologies in ternary copper chalcogenides.

Channeling and Edge Reflections of Surface Polaritons Observed in Star-Shaped WS_2 Islands via sSNOM Imaging

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In most recent years, semiconducting transition metal dichalcogenides (TMDs) such as WS_2 have attracted large interest due to their direct bandgaps, promising optical applications. Chemical vapor deposition (CVD) allows to grow WS_2 islands with controllable size, various shape and large material uniformity. Here, we obtained star-shaped and slightly Mo-doped WS2 islands by adding trace amount of Mo precursor during the growth. Dark-field TEM images and atomic-resolution HAADF-STEM images show that most of the hexagonal star-shaped WS_2 islands are monolayers and composed of six rhombic single grains, with the twisted lattices of neighbor grains. Based on TEM measurements, Mo dopant concentration was estimated as 0.17% and 0.51% near the bisectrix and center region of star-shaped WS_2 islands, respectively. Diffraction limited photoluminescence (PL) images of the islands show multiple domains with unlike optical response, including PL intensity, line-shapes, etc. It is important to reveal local optical properties of as-grown WS_2 islands and the influence of the Mo doped regions on the latter, as well as to correlate the morphology of star-shaped Mo-doped WS_2 islands to PL maps. For this purpose, several complementary optical characterization techniques were applied together, including confocal Raman spectroscopy, PL and scattering Scanning Near-field Optical Microscopy (sSNOM).

AFM images, obtained simultaneously with sSNOM maps, show that the Mo doped diagonal lines have higher AFM height profile, which also appear to have lower intensity in the confocal Raman mapping and PL images. Most interestingly, analysis of the sSNOM maps reveals the channeling effect of WS_2 exciton-polaritons propagating along the bisectrix of star-shaped WS_2 island, as well as making standing waves while reflected by the edges of the island. Dispersion relation of polaritons is obtained by measuring the ripples' period in the bisectrix region and standing waves formed at the edges of different orientation with respect to incident laser beam, under different excitation wavelengths.

The experimental results of various orientation of edges and excitation wavelength fit within the calculated linear dispersion relation of edge launched polaritons. Channeling effect suggests that the Mo-doped lines have a higher polariton density-of-states, compared to the nearby regular WS2 material, which are serving as an “open waveguide”. These findings can lead to fabricating new optoelectronic devices.

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Title:

High-Temperature Superconductor FeSe Films Enabled Through Flux Ratio and Temperature Control

Abstract Body:

FeSe, a bulk superconductor with a T_C of ~9 K has attracted a high level of attention over almost one decade since a skyrocketing boost in T_C was reported for a single unit cell (UC) layer of FeSe grown on $SrTiO_3$(001) by molecular beam epitaxy (MBE) to as high as 100 K. FeSe-$SrTiO_3$ heterostructures have since been fabricated by numerous groups but the record T_C proved extremely difficult to reproduce and thus the mechanism behind it remains concealed. However, after extensive work in the past, the field appears to agree on certain key "ingredients" in the heterostructure sample preparation that are believed essential for the boost in T_C. Those key players are; 1. an ultra-clean substrate surface of a specific double layer of TiO_2 termination typically realized by a chemical and thermal *ex-situ* and additional thermal *in-situ* substrate preparation before growth; 2. ultra-thin – one to few unit cell thickness – limit of FeSe layer thickness; 3. a high number of Se vacancies in the FeSe film ensured through post-growth annealing steps carried out under ultra-high vacuum (UHV) for several hours; 4. followed by a suitable capping layer growth in case films need to be characterized *ex-situ* under ambient pressure due to the rapid oxidation of FeSe in air.

We present our findings on FeSe thin film growth by MBE and present a roadmap for high-T_C – 222 % higher than the reported bulk value in *ex-situ* transport measurements – circumventing above mentioned steps 1, 2, and 3 by simple *in-situ* Se/Fe flux ratio and temperature control during FeSe growth. FeSe films of 20-UC-thickness grown at varying temperatures and Se/Fe flux ratios and the structural and morphological properties of the obtained uncapped FeSe films were analyzed. The morphology of the films showed a sensitive dependence on the growth temperature and flux ratio spanning from perfectly smooth and continuous films with atomic terraces at 450 °C growth temperature and a low flux ratio of 2.5 to exclusively disconnected island growth of large height but smooth top surfaces at lower temperatures and/or higher flux ratios. Surprisingly, the tetragonal P4/nmm crystal structure of β-FeSe was maintained for all investigated films and the *in-situ* observed diffraction pattern in RHEED also maintained the streaky pattern characteristic for smooth FeSe films even for the samples with the most pronounced island growth resulting in a root mean square (RMS) AFM roughness of more than 18 nm. Smaller flux ratios than 2.5 resulted in mixed – β-FeSe/elemental Fe – phase samples. FeSe films grown under optimized conditions at 450 °C and a flux ratio of 2.5 (but without any post-growth UHV anneal) and capped with the commonly used FeTe (300 °C) and elemental Te (room temperature) layers yielded superconducting onset temperatures of about 30 K and a T_C of 20 K.

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