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Heterostructures from Monolayers: van der Waals Heterostructures

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This program has been exceptionally productive, with a successful transition to a 6.1 external program at AFOSR "Hybrid 2D/3D Ferroic Heterostructures for Advanced Electronic Functionalities", one US provisional patent issued and full patent application pending, and 12 publications in high impact factor journals. This program served as the impetus for the formation of the Government Workshop on 2D Materials of the Washington DC Metro Area, and has greatly fostered interactions between ARO, NIST and AFRL. These achievements place NRL's research effort at the forefront of 2D material research worldwide.

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SUMMARY
This program has been exceptionally productive, with a successful transition to a 6.1 external program at AFOSR "Hybrid 2D/3D Ferroic Heterostructures for Advanced Electronic Functionalities", one US provisional patent issued and full patent application pending, and 12 publications in high impact factor journals. This program served as the impetus for the formation of the Government Workshop on 2D Materials of the Washington DC Metro Area, and has greatly fostered interactions between ARO, NIST and AFRL. Work in this program led to the award of the E.O. Hulburt award to Dr. Jonker in 2019 for his leadership and pioneering research in developing 2D materials and heterostructures for advanced functionalities. This program has further enabled development of major new state-of-the art facilities, including a metal-organic chemical vapor deposition system with high purity gas sources for the synthesis of 2D materials such as the transition metal dichalcogenides. These achievements place NRL's research effort at the forefront of 2D material research worldwide.

Technical Objective
The objective of this proposal is to advance a new paradigm for heterostructures unconstrained by lattice match by systematically stacking single monolayers of naturally layered, two dimensional (2-D) materials. We will determine and understand the new electronic and optical properties these heterostructures exhibit, and develop a predictive capability to fabricate them with a property set of our design. The weak interlayer bonding enables a new approach for materials by design through van der Waals epitaxy of non-lattice matched 2-D materials, an avenue not possible with traditional epitaxial approaches dominated by out-of-plane bonding. This represents a bottom up approach towards design and fabrication of new materials that do not exist in nature, and a new class of atomic-scale heterostructures that are expected to exhibit properties and functionality beyond the limits of their bulk counterparts.

Technical Approach
This program brings a diverse set of experts and analytical tools to bear to quickly identify and address the most promising directions – we are well-positioned to fabricate and determine the interactions and properties of these new van der Waals (vdW) heterostructures. We will use a combination of optical, transport and proximal probe measurements to assess how the vdW interaction leads to modification or emergence of new properties, and how one might ultimately implement a "materials by design" strategy to systematically assemble vdW heterostructures for specific functionalities. Our measurements are selected to specifically detect changes induced by vdW interactions, and together with theory enable a route towards a comprehensive understanding.
Sample selection and fabrication. We have developed considerable expertise in large area chemical vapor deposition (CVD) synthesis of the single monolayer building blocks, including

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graphene, MoS_2, WS_2, $MoSe_2$ and others. We will build upon this expertise to synthesize heterostructures from discrete monolayers. Structural properties will be determined by proximal probe and scanning electron microscopies to obtain detailed information on morphology. We have recently demonstrated that atomic force microscopy can directly measure the vdW attractive force from few-layer graphene and MoS_2, and how this force depends upon the number of layers, the electronic structure of the specific material, carrier density and other parameters.

Optical properties. Raman spectroscopy will be used to assess layer thickness, charge doping, and modifications of electronic band structure due to vdW forces. Many of the 2-D materials we will use exhibit a bandgap whose character evolves with layer thickness, and optical excitation / emission provides valuable insight. Reflectivity, photoluminescence (PL), PL excitation spectroscopy, and photoconductivity will be used to determine fundamental properties such as band gap, spin-valley index coupling and relaxation mechanisms. Polarization dependent measurements enable insight into the fundamental properties such as spin-valley index coupling and relaxation mechanisms. Time-resolved and THz spectroscopies determine carrier dynamics, charge transport through the layered structures, and clarify band gaps, band offsets and impurity levels.

Transport properties / electronic structure. Coulomb drag experiments will be used as a tool to measure the magnitude of the electronic coupling between various 2-D materials by comparing the frictional current flow as a function of interlayer distance or separation barrier. We will use our expertise in spin injection to determine spin diffusion across a vdW interface and selectively populate the *K* and *K'* valleys in spin-valley index coupled materials such as MX_2. Both are completely new, would represent significant first-time accomplishments, and provide new insight into the properties of such novel heterostructures. Measurements in which current flows perpendicular to the plane will be performed in tunneling structures. Magnetic contacts will be used to inject spin polarized carriers and detect the resultant spin accumulation. Spin precession techniques will provide quantitative insight into spin lifetimes and relaxation mechanisms. These efforts will be complemented by first principles theory described below.

Theory. Non-lattice matched heterostructures present a challenge requiring a two-step approach to determine the electronic structure. 1) We will determine the atomic and electronic structure of the heterostructure with density functional calculations for selected commensurate cell selections. 2) We will derive a continuum theory for the electronic structure of the heterostructure that will allow arbitrary commensurate cell selections and angles. The optical and transport properties will be computed and compared with experiment.

Technical Progress by FY

FY17

We have fabricated WS_2/graphene/fluorinated graphene (tunnel barrier) non-local spin valve devices and measured the spin relaxation methods as a function of carrier concentrations. We find that the Dyakonov-Perel mechanism is indeed dominant in our unsuspended devices. We find that its strength is at least an order of magnitude higher than in suspended graphene devices, demonstrating that we can impose control over the spin relaxation in graphene

through proximity effects. The spin relaxation mechanism in graphene has been debated for years. Most studies conclude that external impurities rather than intrinsic modes are responsible for spin relaxation in graphene. Studies have shown that elastic scattering in graphene from these extrinsic impurities results in dominant Eliot-Yafet type spin relaxation with the spin relaxation time being proportional to the momentum relaxation time. However, suspended graphene, which is less affected by extrinsic impurities has shown evidence of stronger intrinsic-induced spin relaxation, which is governed by the Dyakonov-Perel mechanism and usually associated with spin orbit coupling, which is very weak in graphene and also mostly attributable to defects and vacancies. Here, the spin relaxation time is inversely proportional to the momentum relaxation time. Control over the spin relaxation is essential in order to fabricate useful spinFET devices from graphene. Theoretical studies have hinted at a method of possible control: create a strong Dyakonov-Perel mechanism in graphene by proximity effect induced spin-orbit coupling. In practice, this can be done by using a WS_2 substrate for a graphene spin valve.

Spin relaxation and proximity effect in WS_2/graphene/fluorographene non-local spin valves. A.L. Friedman, K.M. McCreary, J.T. Robinson, O.M.J. van 't Erve, B.T. Jonker.*Carbon* **131**, 18 (2018).

Single layers of transition metal dichalcogenides (TMDs) are direct gap semiconductors with nondegenerate valley indices. An intriguing possibility for these materials is the use of their valley index as an alternate state variable. Several limitations to such a utility include strong intervalley scattering, as well as multiparticle interactions leading to multiple emission channels. We have previously shown that for single-layer WS_2 films the photoluminescence can be tuned such that emission is from either the neutral or charged exciton (trion). For single layers of CVD grown WS_2 on SiO_2, after excitation with circularly polarized light, the neutral exciton emission has zero polarization, however, the trion emission has a large polarization (28%) at room temperature. In addition, we showed that the trion emission has a unique, non-monotonic temperature dependence that we determined is a consequence of an Auger process that is activated above 100 K. In an attempt to better understand the origin of this mechanism we assembled several heterostructures to change the dielectric environment of the TMD emission including WS_2/Graphene/SiO_2, WS_2/hBN/SiO_2 and hBN/WS_2/hBN/SiO_2. For WS_2/Gr, the anomalous temperature dependence, and hence the Auger activation, is absent.

In 2-D heterostructures with type II band alignment, there is the intriguing possibility of interlayer excitons. These are quasiparticles where Coulomb bound electrons and holes are confined to opposite layers. Such types of excitons should be promising for novel excitonic devices because of unique properties, including a large binding energy, micron-scale in-plane drift-diffusion, and a long population and valley polarization lifetime. While interlayer excitons have been observed, the typical oscillator strength is roughly 200 times lower than for in-plane excitons. We have therefore fabricated MoS_2/WS_2 heterostructures embedded in an optical cavity to try to enhance the out-of-plane component of emission of the exciton. Work is in progress to identify inter-layer exciton emission.

Due to the truly 2-D nature, the optical, electronic, and spintronic properties can be strongly impacted by the surrounding environment. Monolayer TMD materials are typically investigated

in SiO_2/Si substrates, due to the availability and low cost, yet it is becoming increasingly clear that the choice of SiO_2 is detrimentally impacting TMD properties. The van der Waals material, hexagonal boron nitride (hBN), is naturally atomically flat and exhibits low defect density, and may provide an ideal substrate for TMD materials. In practice, two methods may be implemented to achieve a WS_2/hBN heterostructure; 1) sequential transfer of TMDs on hBN or 2) direct synthesis of monolayer TMDs on hBN substrates. We have utilized both techniques to fabricated WS_2/hBN heterostructures. In both cases we find a narrowing of spectral linewidth, when compared to WS_2 supported by SiO_2/Si, suggesting a reduction of external substrate-induced disorder. Temperature-dependent studies of Raman and photoluminescence show distinct differences between sequentially transferred and directly grown heterostructures, indicating differences in the WS_2-hBN interactions, which will be further explored in the future. Furthermore, the reduced linewidth allows us to separately address neutral excitons and trions to better understand fundamental properties.

FY18

We have provided both experimental and theoretical determination of the intrinsic character of interlayer excitons in van der Waals heterostructures (vdWh). In 2-D heterostructures with type II band alignment, there is the intriguing possibility of interlayer excitons. These are quasiparticles where Coulomb bound electrons and holes are confined to opposite layers. Such types of excitons should be promising for novel excitonic devices because of unique properties, including a large binding energy, micron-scale in-plane drift-diffusion, and a long population and valley polarization lifetime. By using advanced preparation techniques, we fabricated MoSe2/WSe2 vdWhs in which we are able to resolve the ILE splitting clearly for the first time, enabling us to elucidate the nature of the ILE and the origin of these features. These ILE peaks have nearly equal intensity, indicating they are of common character, and have *opposite* circular polarizations when excited with circularly polarized light. *Ab initio* calculations successfully account for these observations – they show that both emission features originate from excitonic transitions that are indirect in momentum space and are split by spin-orbit coupling. Also, the electron is strongly hybridized between both the $MoSe_2$and WSe_2 layers, with significant weight in both layers, contrary to the commonly assumed model. Thus, the transitions are not purely interlayer in character. We find that including interlayer hybridization is essential to theoretically determine the ILE character. The hybridized electron eigenstates are superpositions of both spin states, and both spin-orbit split bands are optically bright, decaying optically with holes at the K point with opposite polarizations. This scenario is qualitatively different from previous models and accounts for the roughly equivalent emission intensity of both peaks, and their opposite polarizations. This work represents a significant advance in our understanding of the static and dynamic properties of TMD heterostructures.

Title: Double Indirect Interlayer Exciton in a MoSe2/WSe2 van der Waals Heterostructure
Authors: Aubrey T. Hanbicki, Hsun-Jen Chuang, Matthew R. Rosenberger, C. Stephen Hellberg, Saujan V. Sivaram, Kathleen M. McCreary, I.I. Mazin, and Berend T. Jonker
Type of Publication: Refereed journal
Where it Appeared: ACS Nano, Vol. 12(5), pp. 4719-4726, doi: 10/1021/acsnano.8b01369
Publication Date: April 2018

We have developed a novel nano-squeegee method for the fabrication of van der Waals heterostructures which enables analysis of their intrinsic properties. 2-D materials exhibit many exciting phenomena that make them promising as materials for future electronic, optoelectronic, and mechanical devices. Because of their atomic thinness, interfaces play a dominant role in determining material behavior. In order to observe and exploit the unique properties of these materials, it is therefore vital to obtain clean and repeatable interfaces. However, the conventional mechanical stacking of atomically thin layers typically leads to trapped contaminants and spatially inhomogeneous interfaces, which obscure the true intrinsic behavior. This work presents a simple and generic approach to create clean 2-D material interfaces in mechanically stacked structures. The operating principle is to use an AFM tip to controllably squeeze contaminants out from between 2-D layers and their substrates, similar to a "squeegee". This approach leads to drastically improved homogeneity and consistency of 2-D material interfaces, as demonstrated by AFM topography and significant reduction of photoluminescence line widths. Also, this approach enables emission from interlayer excitons, demonstrating that the technique enhances interlayer coupling in van der Waals heterostructures. The technique enables repeatable observation of intrinsic 2-D material properties, which is crucial for the continued development of these promising materials.

Title: Nano-'Squeegee' for the Creation of Clean 2D Material Interfaces,
Authors: M. R. Rosenberger, Hsun-Jen Chuang, K. M. McCreary, A.T. Hanbicki, S.V. Sivarum and B. T. Jonker
Type of Publication: Refereed journal
Where it Appeared: ACS Applied Materials & Interfaces, Vol. 10(12), pp. 10379-0387, doi: 10.1021/acsami.8b01224
Publication Date: February 2018

We have determined the electrical character of defects occurring in WS_2 / graphene van der Waals heterostructures (vdWhs), correlated their density with optical properties, and developed a model which provides good agreement with the experimental data. The properties of TMDs are expected to be strongly influenced by a variety of defects which result from growth procedures and/or fabrication. Despite the importance of understanding defect-related phenomena, there remains a need for quantitative nanometer-scale characterization of defects over large areas in order to understand the relationship between defects and observed properties, such as photoluminescence (PL) and electrical conductivity. We fabricated WS_2 / graphene vdWs using the nano-squeegee approach described above in which the graphene serves as a conductive back plane. We used conductive atomic force microscopy (CAFM) to directly observe defects and determine their electrical character. The observed defects are highly conductive when probed out-of-plane with CAFM, which enables precise identification of defect locations and direct quantification of areal defect density. We find that the defect density ranges from 2.3×10^{10} cm^{-2} to 4.5×10^{11} cm^{-2} in our samples. We correlate the measured defect density with spatial variations in photoluminescence (PL) and observe a pronounced inverse relationship between PL intensity and defect density. We propose a model in which the observed electronically active defects serve as nonradiative recombination centers and obtain good agreement with the experimental data. These results provide critical information for understanding the cause of spatial variations in TMD properties and are a significant step toward optimization of TMD materials for future applications.

Title: Electrical Characterization of Discrete Defects and Impact of Defect Density on Photoluminescence in Monolayer WS2
Authors: M. R. Rosenberger, Hsun-Jen Chuang, K. M. McCreary, C. H. Li, and B. T. Jonker
Type of Publication: Refereed journal
Where it Appeared: ACS Nano, Vol. 12(2), pp. 1793-1800, doi: 10.1021/acsnano.7b08566
Publication Date: January 2018

Combining single-layer transition metal dichalcogenides (SL TMDs) with other 2-D materials in van der Waals heterostructures offers an intriguing means of controlling the electronic properties through many-body effects via engineered interlayer interactions. We have employed micro-focused angle-resolved photoemission spectroscopy (microARPES) and in-situ surface doping to manipulate the electronic structure of SL WS_2 on hexagonal boron nitride (WS_2/h-BN). The h- BN substrate greatly improves the electronic structure quality obtained from SL WS_2, with 300% sharper ARPES spectral features as compared to SL WS_2 directly interfaced with the supporting oxide substrate. Upon electron doping, we observe an unexpected giant renormalization of the SL WS_2 valence band (VB) spin-orbit splitting from 430 meV to 660 meV, together with a band gap reduction of at least 325 meV, attributed to the formation of trionic quasiparticles. These findings suggest that the electronic, spintronic and excitonic properties are widely tunable in 2-D TMD/h-BN heterostructures, as these are intimately linked to the quasiparticle dynamics of the materials.

Title: Giant Spin-Splitting and Band Renormalization in Single-Layer WS2/h-BN Heterostructures
Authors: J. Katoch, S. Ulstrup, R. J. Koch, S. Moser, K. M. McCreary, S. Singh, J. Xu, B. T. Jonker, R. K. Kawakami, A. Bostwick, E. Rotenberg, and C. Jozwiak
Type of Publication: Refereed journal
Where it Appeared: Nature Physics, doi: 10.1038/s4156-017-0033-4
Publication Date: January 2018

FY19

The mechanisms leading to spin relaxation in graphene and its heterostructures continue to be debated. Control of the spin relaxation in graphene-based structures is necessary to achieve the envisioned utility of graphene in future spintronic devices beyond Moore's law. Proximity induced spin relaxation caused by contact to a high spin-orbit material, such as WS2, offers a promising avenue to manipulate the spin lifetime. We demonstrate the operation of WS2/graphene/fluorographene non-local spin valves and extract the spin lifetimes for a range of carrier concentrations by Hanle effect measurements. Four-terminal charge transport measurements allow us to calculate the momentum relaxation time as a function of carrier concentration and compare it to the spin lifetime. These data show that the D'yakonov-Perel' mechanism is the dominate spin relaxation mechanism for WS2/graphene/fluorographene devices, while the Elliot-Yafet mechanism is the dominant spin relaxation mechanism for reference graphene/fluorographene devices. We attribute the change in spin relaxation type in part with the inclusion of WS2 as a substrate to proximity induced spin-orbit coupling due to the adjacent WS2 layer, and we compare our data to previous examples of spin relaxation studies in graphene devices.

Title: Spin relaxation and proximity effect in WS2/graphene/fluorographene non-local spin valves
Authors: A.L. Friedman, K.M. McCreary, J.T. Robinson, O.M.J. van 't Erve, B.T. Jonker,
Type of Publication: Refereed journal
Where it Appeared: Carbon 131, 18-25 (May 2018) https://doi.org/10.1016/j.carbon.2018.01.080
Publication Date: May 2018

The electronic properties of devices based on two-dimensional materials are significantly influenced by interactions with the substrate and electrode materials. Here, we use photoemission electron microscopy with collaborators at the Advanced Light Source at the Lawrence Berkeley National Laboratory to investigate the real- and momentum-space electronic structures of electrically contacted single-layer WS2 stacked on hBN, SiO2, and TiO2 substrates. Using work function and X-ray absorption imaging, we single-out clean microscopic regions of each interface type and collect the valence band dispersion. We infer the alignments of the electronic bandgaps and electron affinities from the measured valence band offsets of WS2 and the three substrate materials using a simple electron affinity rule and discuss the implications for vertical band structure engineering using mixed three- and two-dimensional materials.

Title: Imaging microscopic electronic contrasts at the interface of single-layer WS2 with oxide and boron nitride substrate
Authors: Soren Ulstrup, Roland J. Koch, Daniel Schwarz, Kathleen M. McCreary, Berend T. Jonker, Simranjeet Singh, Aaron Bostwick, Eli Rotenberg, Chris Jozwiak, and Jyoti Katoch
Type of Publication: Refereed journal
Where it Appeared: Appl. Phys. Lett. 114, (16 April 2019). DOI: 10.1063/1.5088968
Publication Date: April 2019

Single photon emitters (SPEs), or quantum emitters, are key components in a wide range of nascent quantum-based technologies, including computing, communications, sensing and metrology. Recent work has identified SPE behavior occurring at seemingly random sites in single monolayer transition metal dichalcogenides (TMDs) such as WSe_2. However, the origin of the SPE process is not understood, and there was no control over the creation and spatial location of such sites. We have developed a new method for encoding strain into two dimensional materials (2DM) to create and deterministically place SPEs in arbitrary locations with nanometer-scale precision. Our material platform consists of a 2DM placed on top of a deformable polymer film. Upon application of sufficient mechanical stress using an atomic force microscope tip, the 2DM/polymer composite deforms, resulting in formation of highly localized strain fields with excellent control and repeatability. We show that SPEs are created and localized at these nanoindents, and exhibit single photon emission up to 60K, the highest temperature reported in these materials. This ***quantum calligraphy*** allows deterministic placement and real time design of arbitrary patterns of SPEs for facile coupling with photonic waveguides, cavities and plasmonic structures. In addition to enabling versatile placement of SPEs, these results present a general methodology for imparting strain into 2DM with nanometer-scale precision, providing an invaluable tool for further investigations and future applications of strain engineering of 2DM and 2DM devices.

Title: Quantum Calligraphy: Writing Single-Photon Emitters in a Two-Dimensional Materials Platform
Authors: M.R. Rosenberger, C. K. Dass, H.J. Chuang, S.V. Sivaram, K.M. McCreary, J.R. Hendrickson and B.T. Jonker
Type of Publication: Refereed journal
Where it Appeared: ACS Nano 13, 904-912 (January 2019). DOI: 10.1021/acsnano.8b08730
Publication Date: January 2019

FY20 Close out

Second order nonlinear processes such as second harmonic generation (SHG) originate from noncentrosymmetric crystal structure and have been widely used for the determination of layer

number, crystal orientation, and twist angle of atomically thin materials. Nonlinear microscopy can provide direct imaging of symmetry-related local information such as crystal domains, strain fields, edge disorders, etc. We report continuous-wave second harmonic and sum frequency generation from two-dimensional transition metal dichalcogenide monolayers and their heterostructures with pump irradiances several orders of magnitude lower than those of conventional pulsed experiments. The high nonlinear efficiency originates from above-gap excitons in the band nesting regions, as revealed by wavelength-dependent second order optical susceptibilities quantified in four common monolayer transition metal dichalcogenides. Using sum frequency excitation spectroscopy and imaging, we identify and distinguish one- and two-photon resonances in both monolayers and heterobilayers. Data for heterostructures reveal responses from constituent layers accompanied by nonlinear signal correlated with interlayer transitions. We demonstrate spatial mapping of heterogeneous interlayer coupling by sum frequency and second harmonic confocal microscopy on heterobilayer MoSe2/WSe2.

Continuous Wave Sum Frequency Generation and Imaging of Monolayer and Heterobilayer 2D Semiconductors, K. Yao, E. Yanev, H.-J. Chuang, M.R. Rosenberger, X. Xu, T. Darlington, K.M. McCreary, A.T. Hanbicki, K. Watanabe, T. Taniguchi, B.T. Jonker, X. Zhu, D. Basov, J. Hone, J.P. Schuck, *ACS Nano* 14, 708-714 (31 Dec 2019) NRL release # 19-1231-3629. NRL/JA/6390/19/420

The band structure of transition metal dichalcogenides (TMDs) has unique features that make them ideal candidates for valleytronics, a field where the valley index is a potential new state variable. The low-dimensional hexagonal lattice structure of TMDs, combined with strong orbital hybridization and time-reversal symmetry, results in two inequivalent, high symmetry points, K/K', with coupled spin and valley indices and unique optical selection rules. An imbalance in the carrier population between the K/K' valleys, referred to as a valley polarization (VP), can, therefore, be created under excitation with circularly polarized light, enabling the independent initialization and addressing of the valley index. We examine different cases of heterostructures consisting of WS2 monolayers grown by chemical vapor deposition as the optically active material. We show that the degree of valley polarization of WS2 is considerably influenced by the material type used to form the heterostructure. Our results suggest that the interaction between WS2 and graphene (WS2/Gr) has a strong effect on the temperature dependent depolarization (i.e., decrease in polarization with increasing temperature), with polarization degrees reaching 24% at room temperature under near-resonant excitation. This contrasts with hBN-encapsulated WS2, which exhibits a room temperature polarization degree of only 11%. The observed low depolarization rate in the WS2/Gr heterostructure is attributed to the nearly temperature independent scattering rate due to phonons and fast charge and energy transfer processes from WS2 to graphene. Significant variations in the degree of polarization are also observed at 4K between the different heterostructure configurations. Intervalley hole scattering in the valence band proximity between the K and C points of WS2 is sensitive to the immediate environment, leading to the observed variations.

Prominent room temperature valley polarization in WS2/graphene heterostructures grown by chemical vapor deposition, I. Paradisanos , K. M. McCreary , D. Adinehloo, L. Mouchliadis, J. T. Robinson, Hsun-Jen Chuang, A. T. Hanbicki , V. Perebeinos, B. T. Jonker, E. Stratakis, and G. Kioseoglou ; Appl. Phys. Lett. 116, 203102 (May 2020);

https://doi.org/10.1063/5.0002396. NRL/JA/6390/19/479

Van der Waals layered materials, such as transition metal dichalcogenides (TMDs), are an exciting class of materials with weak interlayer bonding which enables one to create so-called van der Waals heterostructures (vdWH). One promising attribute of vdWH is the ability to rotate the layers at arbitrary azimuthal angles relative to one another. Recent work has shown that control of the twist angle between layers can have a dramatic effect on TMD vdWH properties, but the twist angle has been treated solely through the use of rigid-lattice moiré patterns. No atomic reconstruction, *i.e.* any rearrangement of atoms within the individual layers, has been reported experimentally to date. Here we demonstrate that vdWH of $MoSe_2/WSe_2$ and MoS_2/WS_2 at twist angles ≤ 1° undergo significant atomic level reconstruction leading to discrete commensurate domains divided by narrow domain walls, rather than a smoothly varying rigid-lattice moiré pattern as has been assumed in prior experimental work. Using conductive atomic force microscopy (CAFM), we show that TMD vdWH at small twist angles exhibit large domains of constant conductivity. The domains in samples with R-type stacking are triangular, while the domains in samples with H-type stacking are hexagonal. Transmission electron microscopy provides additional evidence of atomic reconstruction in $MoSe_2/WSe_2$ structures and demonstrates the transition between a rigid-lattice moiré pattern for large angles and atomic reconstruction for small angles. We use density functional theory to calculate the band structures of the commensurate reconstructed domains, and find that the modulation of the relative electronic band edges is consistent with the CAFM results and photoluminescence spectra. The presence of atomic reconstruction in TMD heterostructures and the observed impact on nanometer-scale electronic properties provides fundamental insight into the behavior of this important class of heterostructures.

Twist angle dependent atomic reconstruction and moiré patterns in transition metal dichalcogenide van der Waals heterostructures, Matthew R. Rosenberger, Hsun-Jen Chuang, Madeleine Phillips, Vladimir P. Oleshko, Kathleen M. McCreary, Saujan V. Sivaram, C. Stephen Hellberg, and Berend T. Jonker, ACS Nano 14 (4), 4550-4558 (13 March 2020) https://dx.doi.org/10.1021/acsnano.0c00088 . NRL/JA/6390/19/396

Stacking two-dimensional (2D) van der Waals materials with different interlayer atomic registry in a heterobilayer causes the formation of a long-range periodic superlattice that may bestow the heterostructure with properties such as new quantum fractal states or superconductivity. Recent optical measurements of transition metal dichalcogenide (TMD) heterobilayers have revealed the presence of hybridized interlayer electron-hole pair excitations at energies defined by the superlattice potential. The corresponding quasiparticle band structures, so-called minibands, have remained elusive, and no such features have been reported for heterobilayers composed of a TMD and another type of 2D material. We introduce a new x-ray capillary technology for performing microfocused
angle-resolved photoemission spectroscopy with a spatial resolution of ~1 □m, and directly observe minibands at certain twist angles in mini Brillouin zones (mBZs). We discuss their origin in terms of initial and final state effects by analyzing their dispersion in distinct mBZs.

Direct observation of minibands in twisted heterobilayers, Søren Ulstrup, Roland J. Koch,

Simranjeet Singh, Kathleen M. McCreary, Berend T. Jonker, Jeremy T. Robinson, Chris Jozwiak, Eli Rotenberg, Aaron Bostwick, Jyoti Katoch and Jill A. Miwa, *Science Advances* 6, 6104 (3 Apr 2020) DOI: 10.1126/sciadv.aay6104. NRL Release 19-1231-1469; STRN NRL/JA/6390/19/181

Patents

- A nano-indent process for creating single photon emitters in a two-dimensional materials platform"; Navy Case No. 111452-US2

Transitions to external programs:

- Hybrid 2D/3D Ferroic Heterostructures for Advanced Electronic Functionalities, funded by AFOSR. NRL JON 63-1P54

Awards

- NRL E.O. Hulburt award to B.T. Jonker for his leadership and pioneering research in developing 2D materials and heterostructures for advanced functionalities.

Selected Invited talks:

Understanding and Controlling Light Emission in Two-Dimensional Materials: Intrinsic Defects and Extrinsic Perturbations; Penn State Graphene and Beyond Workshop; May 9, 2019; NRL/OP/6390/19/200

Quantum Calligraphy: Writing Single-Photon Emitters in a Two-Dimensional Materials Platform; 2019 AVS Conference; October 23, 2019; NRL/OP/6390/19/110

Quantum Calligraphy—Writing Single Photon Emitters in a Two-Dimensional Materials Platform; 2019 MRS Fall Meeting; December 2, 2019; Rosenberger, M. R.; Dass, C. K.; Chuang, H.-J.; Sivaram, S. V.; McCreary, K. M.; Hendrickson, J. R.; Jonker, B. T. ; NRL/OP/6390/19/110

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