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Functional Domain Walls as Active Elements for Energy Technology

Final Technical Report for the Period July 14, 2011 - July 14, 2016

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Junqiao Wu

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ABSTRACT

In the past five years in the duration of this project (July 2011-July 2016), we have made a wide range of achievements in both basic research and energy applications along the direction planned in the original proposal. These achievements were reflected by 13 articles published in peer-reviewed journals including *Nature Communications*, *Nano Letters*, etc., and one currently in revision at *Science*. These papers have been accumulatively cited for more than 660 times as of October 2016, according to Web of Science statistics.

Specifically, we have made impactful discoveries in the following fields.

<u>Basic Research</u>. We have investigated in depth the materials physics of the representative quantum material, VO2, on which most of our project is anchored. We have discovered that independent diffusion of heat and charge in the absence of quasiparticles in metallic $VO_2$ leads to an anomalously low electronic thermal conductivity, dramatically violating the Wiedemann-Franz law, which is a robust law governing behavior of normal conductors stating that free electrons transport heat proportionally to the charge they transport. In addition, we have discovered a peculiar thermal rectification effect based on its phase transition, as well as a gating response of the phase transition. In parallel to the work on VO2, we have also made breakthroughs in investigation of transition metal dichalcogenides (TMDs): we have experimentally demonstrate a strong anisotropy in in-plane thermal conductivity of black phosphorous, discovered a new, unusual member of the TMDs family, ReS2, where the bulk behaves as monolayers due to electronic and vibrational decoupling, unusual interaction between physi-sorbed molecules and 2D semiconductors, and thermally driven crossover from indirect toward direct bandgap in some 2D TMDs.

<u>Applications</u>. Based on the understanding and knowledge gained from the basic investigation, we have developed novel tools and devices for energy applications. These include a nanowire based microthermometer for quantitative evaluation of electron beam heating in electron microscopy, giant-amplitude, high-work density microactuators and torsional micromuscles, as well as nanoscale thermometers and powermeters, all based on the VO2 phase transition.

Details of each of these works are described in the attached file.

BASIC RESEARCH

1) Anomalously low electronic thermal conductivity in metallic vanadium dioxide. Pending at Science (2016).

In electrically conductive solids, the Wiedemann-Franz law requires the electronic contribution to thermal conductivity to be proportional to electrical conductivity. This law reflects a basic property of Fermi liquids in which charge and heat are both transported by the same quasiparticles. Violations of the Wiedemann-Franz law are typically an indication of unconventional quasiparticle dynamics, such as inelastic scattering or hydrodynamic collective motion of charge carriers typically significant only at cryogenic temperatures. We report a drastic breakdown of the Wiedemann-Franz law at high temperatures ranging from 240 to 340 K, with an order of magnitude of decrease in the electronic thermal conductivity in metallic vanadium dioxide in the vicinity of its metal-insulator transition. Different from previously established mechanisms, the unusually low electronic thermal conductivity is a signature of the absence of quasiparticles in a strongly correlated electron fluid where heat and charge diffuse independently.

2) Modulating Photoluminescence of Monolayer Molybdenum Disulfide by Metal-Insulator Phase Transition in Active Substrates. This work was published at Small, 12, 3976 (2016).

The atomic thickness and flatness allow properties of 2D semiconductors to be modulated with influence from the substrate. Reversible modulation of these properties requires an "active," reconfigurable substrate, i.e., a substrate with switchable functionalities that interacts strongly with the 2D overlayer. In this work, the photoluminescence (PL) of monolayer molybdenum disulfide (MoS2 ) is modulated by interfacing it with a phase transition material, vanadium dioxide (VO 2 ). The MoS2 PL intensity is enhanced by a factor of up to three when the underlying VO 2 undergoes the thermally driven phase transition from the insulating to metallic phase. A nonvolatile, reversible way to rewrite the PL pattern is also demonstrated. The enhancement effect is attributed to constructive optical interference when the VO2 turns metallic. This modulation method requires no chemical or mechanical processes, potentially finding applications in new switches and sensors.

3) Demonstration of anisotropy in in-plane thermal conductivity of black phosphorous. Published at Nature Commun. 6, 8573 (2015).

Black phosphorus (BP) attracts enormous research attention as a promising material for electronic, optoelectronic and thermoelectric applications. We discovered large anisotropy in in-plane thermal conductivity ($\kappa$) of single crystal BP nanoribbons along the zigzag (ZZ) and armchair (AC) lattice directions at variable temperatures. $\kappa$ measurements were carried out under the condition of steady state longitudinal heat flow using suspended-pad micro-devices. We discovered increasing $\kappa$ anisotropy, up to a factor of two, with temperatures above 100K. A size effect in $\kappa$ was also observed in which thinner nanoribbons show lower $\kappa$, while the anisotropy ratio stays around two within the investigated thickness range. Based on the Boltzmann transport model, the high anisotropy is attributed to anisotropic group velocity of acoustic phonons. Our results that reveal the intrinsic, orientation-dependent $\kappa$ of BP are useful for designing BP-based devices, as well as understanding of fundamental physical properties of layered materials.

4) Discovery of monolayer behavior in bulk $ReS_2$ due to electronic and vibrational decoupling. Published at Nature Communications, 5, 3252 (2014).

This work presents a new and unique member in the layered semiconductor family, rhenium disulphide ($ReS_2$), where each layer is electronically and vibrationally decoupled from neighboring layers, and as such, its bulk behaves almost as isolated monolayers.

Such vanishing inter-layer coupling enables probing of two-dimensional (2D) systems without the need for monolayers. Therefore, $ReS_2$ bulk crystals would be an ideal platform to probe 2D excitonic and lattice physics, circumventing the challenge of preparing large-area, single-crystal monolayers. A wide range of 2D experiments are currently severely limited by the availability of large-area monolayers or by low sensitivity to monolayer thickness, such as photoelectron spectroscopy, hydrostatic pressure in diamond anvil cells, and heterojunction electronics; but following our work, they become possible and relatively easy on the $ReS_2$ bulk. In this sense, the presented results introduce a new type of semiconducting transition metal dichalcogenides (sTMDs) with distinct physical properties from conventional members of the sTMDs explored to date.

More specifically, sTMDs consist of 2D layers held together by weak forces where the layers are electronically and vibrationally coupled. Isolated monolayers show changes in electronic structure and lattice vibration energies, including a transition from indirect to direct bandgap. In this work, we present $ReS_2$ as a new member of the sTMD family, where such variation is absent and the bulk behaves as electronically and vibrationally decoupled monolayers stacked together. From bulk to monolayers, $ReS_2$ remains direct bandgap, and its Raman spectrum shows no dependence on the number of layers. Inter-layer decoupling is further demonstrated by the insensitivity of the optical absorption and Raman spectrum to inter-layer distance modulated by hydrostatic pressure. Density Functional Theory calculations attribute the decoupling to an in-plane Peierls distortion of the 1T structure of $ReS_2$ layers away from the perfect honeycomb structure, which prevents ordered inter-layer stacking and minimizes the inter-layer overlap of electron wavefunctions.

From a fundamental science point of view, our work re-defines the “2D-ness” of semiconductors by the inter-layer coupling strength, as opposed to the virtual dimensionality of the crystal. We show the important consequence of in-plane structural distortion of layered semiconductors in their electronic and vibrational behavior. As such distortion might be stabilized by different means, e.g., mechanically, chemically or electrostatically, this opens the opportunity for realizing new 2D systems without physical isolation or synthesis of atomic layers.

5) <u>Direct observation of nanoscale Peltier and Joule effects at metal-insulator domain walls in vanadium dioxide nanobeams.</u> Published in Nano Letters 14, 2394(2014).

The metal to insulator transition (MIT) of strongly correlated materials is subject to strong lattice coupling which brings about the unique one-dimensional alignment of metal-insulator (M-I) domains along nanowires or nanobeams. Many studies have investigated the effects of stress on the MIT and hence the phase boundary, but few have directly examined the thermal effect across the metal-insulating interface.

In this work, we use thermoreflectance microscopy to create two-dimensional temperature maps of single-crystalline $VO_2$ nanobeams under external electrical bias in the phase coexisting regime. We directly observe highly localized, alternating Peltier heating and cooling as well as Joule heating concentrated at the M-I domain boundaries, indicating the significance of the junction depletion region and the domain walls. Utilizing the thermoreflectance technique, we are able to elucidate strain accumulation along the nanobeam and distinguish between two insulating phases of $VO_2$ through detection of the opposite polarity of their respective thermoreflectance coefficients. Microelasticity theory was employed to predict favorable domain wall configurations, confirming the monoclinic phase identification. The insight gained through thermoreflectance imaging and the ability to distinguish between insulating phases illuminate the underlying impact of stress on the nanobeam, while examination of the elastic energy determines the favored wall configurations to minimize the total elastic strain for each monoclinic phase.

6) A thermal rectifier based on phase transition. Published at Nano Lett. 14, 4867 (2014).

Heat flow control is essential for widespread applications of heating, cooling, energy conversion and utilization. In collaboration with colleagues, we demonstrated the observation of temperature-gated thermal rectification in vanadium dioxide nanobeams, in which an environment temperature actively modulates asymmetric heat flow. In this three terminal device, there are two switchable states, which can be accessed by global heating: “Rectifier” state and “Resistor” state. In the “Rectifier” state, up to 22% thermal rectification is observed. In the “Resistor” state, the thermal rectification disappears. This temperature-gated rectifier can have substantial implications ranging from autonomous thermal management of micro/nanoscale devices to thermal energy conversion and storage.

7) Stable p- and n-type doping of few-layer graphene/graphite . Published at Carbon, 57, 507 (2013).

ZnMg and NbCl5 were intercalated in graphite and the presence of such molecules between the graphene sheets results in n- and p-type doping, respectively. The doping effect is confirmed by Hall and Raman measurements and the intercalation process is monitored by scanning tunneling microscopy. After intercalation the carrier concentration increase almost an order of magnitude and reaches values as high as 10^19and 10^18 /cm^3 for p and n-type doping, respectively. For higher intercalation times, the intercalated graphite turns back to be as ordered as pristine one as evidenced by the reduction in the D peak in Raman measurements. Intercalation compounds show remarkable stability allowing us to permanently tune the physical properties of few-layer graphite. Our study has provided a new route to produce stable and functional graphite intercalation compounds and the results can be applied to other graphitic structures such as few-layer graphene on SiC.

8) Unusual interaction between physi-sorbed molecules and 2D semiconductors. Published at Nano Lett. 13, 2831 (2013).

In the monolayer limit, transition metal dichalcogenides become direct-bandgap, light emitting semiconductors. The quantum yield of light emission is low and extremely sensitive to the substrate used, while the underlying physics remains elusive. We discovered over 100 times modulation of light emission efficiency of these two-dimensional semiconductors by physical adsorption of $O_2$ and/or $H_2O$ molecules, while inert gases do not cause such effect. The $O_2$ and/or $H_2O$ pressure acts quantitatively as an instantaneously reversible “molecular gating” force, providing orders of magnitude broader control of carrier density and light emission than conventional electric field gating. Physi-sorbed $O_2$ and/or $H_2O$ molecules electronically deplete n-type materials such as $MoS_2$ and $MoSe_2$, which weakens electrostatic screening that would otherwise destabilize excitons, leading to the drastic enhancement in photoluminescence. In p-type materials such as $WSe_2$, the molecular physi-sorption results in the opposite effect. Unique and universal in two-dimensional semiconductors, the effect offers a new mechanism for modulating electronic interactions and implementing optical devices.

9) Thermally driven crossover from indirect toward direct bandgap in 2D semiconductors. Published at Nano Lett., 12, 5576 (2012).

Layered semiconductors based on transition-metal chalcogenides usually cross from indirect bandgap in the bulk limit over to direct bandgap in the quantum (2D) limit. Such a crossover can be achieved by peeling off a multi-layer sample to a single layer. For exploration of physical behavior and device applications, it is much desired to reversibly modulate such crossover in a multi-layer sample. Here we demonstrate that in a multi-layer sample where the indirect bandgap and direct bandgap are nearly degenerate, temperature rise can effectively drive the system toward the 2D limit by thermally decoupling neighboring layers via interlayer thermal expansion. Such a situation is realized in few-layer $MoSe_2$, which shows stark contrast from the well explored $MoS_2$ where the indirect and direct bandgaps are far from degenerate. Photoluminescence of few-layer $MoSe_2$ is much enhanced with the temperature rise, much like the way that the photoluminescence is enhanced due to the bandgap crossover going from the bulk to the quantum limit, offering potential applications involving external modulation of optical properties in 2D semiconductors. The direct bandgap of $MoSe_2$, identified at 1.55 eV, may also promise applications in energy conversion involving solar spectrum, as it is close to the optimal bandgap value of single-junction solar cells and photoelechemical devices.

10) Gated metal-insulator transition. Published at Appl. Phys. Lett., 99, 062114 (2012).

By gating single-crystal $VO_2$ nanowires using $HfO_2$ as the dielectric, we observed field-effect modulation of the $VO_2$ conductance and an associated memory effect. We observe a change in conductance (~6%) of our devices induced by gate voltage when the system is in the insulating phase. The response is reversible and hysteretic, and the area of hysteresis loop becomes larger as the rate of gate sweep is slowed down. A phase lag exists between the response of the conductance and the gate voltage, indicating the existence of a memory of the system.

APPLICATIONS

11) Vanadium dioxide nanowire-based microthermometer for quantitative evaluation of electron beam heating. Published at Nature Commun., 5, 4986 (2014).

Temperature measurement is critical for many technological applications and scientific experiments, and different types of thermometers have been developed to detect temperature at macroscopic length scales. However, quantitative measurement of the temperature of nanostructures remains a challenge. Here, we show a new type of microthermometer based on a vanadium dioxide nanowire. Its mechanism is derived from the metal–insulator transition of vanadium dioxide at 68 $^{o}$C. As our results demonstrate, this microthermometer can serve as a thermal flow meter to investigate sample heating from the incident electron beam using a transmission electron microscope. Owing to its small size the vanadium dioxide nanowire-based microthermometer has a large measurement range and high sensitivity, making it a good candidate to explore the temperature environment of small spaces or to monitor the temperature of tiny, nanoscale objects.

12) Demonstration of powerful, multifunctional torsional micromuscles activated by phase transition. Published at Advanced Materials. 26, 1746 (2014).

Torsional artificial muscles are difficult to scale down to the micro scale, especially if robust and diverse functionalities are to be integrated inside a very limited space. Miniaturisation of conventional rotary motors is a great challenge because of their complex design. Piezoelectric ultrasonic micro-motor is a successful alternative although its size is still on the millimetre scale. Further scaling down requires to pursue different designs. Although an electrostatically driven microelectromechanical motor was developed twenty years ago, its inherently on-chip structure complicates the integration to drive other devices. Similar mechanism was used to develop carbon nanotube based nanoelectromechanical actuators. Rotary magnetic field was also utilized to actuate the rotation of micro magnetic metal paddles. Torsional muscles using sole or guest-filled twisted carbon nanotube yarns were recently reported. These micro or nanoscale motors, however, all deliver a single function, *i.e.*, torsional motion. For micro-robots in simulation of living organisms, it is much desired to have a micro torsional muscle integrating multifunctions in a limited space, such as simultaneous actuation and sensing. In addition, higher power density, larger rotation amplitude, and higher rotational speed are desired in these applications.

$VO_2$ emerges as an ideal driving material for multifunctional artificial muscles, owing to its simultaneously high Young's modulus (~140 GPa), high transformation strain (1~2% in single crystals), and intrinsically fast speed (~picosecond) in its metal-insulator transition (MIT) at ~ 68 °C. Its volume work density is up to 7 J/cm$^3$, which is two orders of magnitude higher than piezoceramics and 3 orders higher than human muscles. Although $VO_2$ based linear and bending actuators have been demonstrated by groups including ours, development of torsional ones is still a great challenge. In this work we demonstrate a micro torsional muscle driven by the phase transition of $VO_2$, with a simple design but superior performance in power density, rotation amplitude, and rotational speed. The artificial muscle also combines all the functions including torsional actuator, memristor, and proximity sensor, showing great potential in applications that require a high level of functionality integration in a small space.

13) <u>Giant-Amplitude, High-Work Density Microactuators with Phase Transition Activated Nanolayer Bimorphs.</u> Published at Nano Lett. 12, 6302 (2012).

Various mechanisms are currently exploited to transduce a wide range of stimulating sources into mechanical motion. At the microscale, simultaneously high amplitude, high work output, and high speed in actuation are hindered by limitations of these actuation mechanisms. Here we demonstrate a set of microactuators fabricated by a simple microfabrication process, showing simultaneously high performance by these metrics, operated on the structural phase transition in vanadium dioxide responding to diverse stimuli of heat, electric current, and light. In both ambient and aqueous conditions, the actuators bend with exceedingly high displacement-to-length ratios up to in the sub-100 μm length scale, work densities over 0.63 J/cm$^3$, and at frequencies up to 6 kHz. The functionalities of actuation can be further enriched with integrated designs of planar as well as three-dimensional geometries. Combining the superior performance, high durability, diversity in responsive stimuli, versatile working environments, and microscale manufacturability, these actuators offer potential applications in microelectromechanical systems, microfluidics, robotics, drug delivery, and artificial muscles.

14) <u>Applications: nanoscale thermometer and powermeter.</u> Published at ACS Nano, 5, 10102 (2011).

We have developed nanoscale, solid-state thermometers and powermeters by exploiting the thermally driven phase transition in $VO_2$ nanowires near room temperature. It is well known that quantitative thermal characterization is difficult at the nanoscale. Utilizing the sharp phase transition of $VO_2$ at a well defined temperature, and the stark change in optical reflection between the two phases, we developed a strategy to measure temperature and heat flow in systems of sub-micron sizes. As a first example, we used this strategy to gauge heat transfer across the interface between nanoscale solids and gas. When solid materials and devices scale down in size, heat transfer from the active region to the gas environment becomes increasingly significant. We show that the heat transfer coefficient across the solid-gas interface behaves very differently when the size of the solid is reduced to the nanoscale.