Quasi 2D and 1D van der Waals Materials – Properties and Device Applications

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Highlights or Research Activities in NDL and POEM Center

Graphene thermal field and thermal management
- The MRS Medal

Quazi-1D van der Waals materials
- The Vannevar Buch Faculty Fellow
- NSF DMREF; DOD ONR

Nanoscale phonon engineering
- IEEE Pioneer of Nanotechnology Award
- DOE EFRC Ultra

Raman and Brillouin-Mandelstam spectroscopy
- The Brillouin Medal
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Department of Energy (DOE) contract DE-SC0021020 Physical Mechanisms and Electric-Bias Control of Phase Transitions in Quasi-2D Charge-Density-Wave Quantum Materials
UCR PI: A.A. Balandin

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Outline of the Talk

→ Definitions and Motivations: Quasi-1D and 2D van der Waals materials
→ Properties and applications of quasi-1D van der Waals materials
→ Current conduction of quasi-1D bundles
→ Electromagnetic interference shielding
→ Quasi-2D Charge-density-wave devices
→ Radiation hardness
→ Mechanism of switching
→ The “narrow band noise”
→ Conclusions
Terminology: Van der Waals Materials

- **Quasi-2D van der Waals Materials**
- **Quasi-1D van der Waals Materials**

- **MoS$_2$**
- **TaSe$_3$ atomic threads**

- Crystal structure of monoclinic TaSe$_3$, with alternating layers of TaSe$_3$
- Cross section of the unit cell, perpendicular to the chain axis (b axis).
- The side view: 1D nature of TaSe$_3$ chains along the b axis.
The Meaning of “Quasi” and “Quantum”

→ “Quasi” in a sense of a bundle

→ “Quasi” in a sense that you may have weaker covalent bonds in perpendicular plane

→ “Quantum” in a sense of quantum confinement: it can reveal itself differently for van der Waals materials

→ “Quantum” is relation to the charge-density-wave phases

TaSe$_3$
Material Synthesis: Chemical Vapor Transport (CVT) or Chemical Vapor Deposition (CVD)


Secondary electron image of a TaSe$_3$ nanowire produced by solvent exfoliation.
Fabrication of Quasi-1D and Quasi-2D Devices

E-Beam Lithography

Shadow Mask Method


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Quasi-1D Channel TaSe$_3$ Devices Fabricated by Electron Beam Lithography

Quasi-1D bundles and BN capping

Schematic of the TaSe$_3$/h-BN quasi-1D / quasi-2D nanowire heterostructures used for the I-V testing.

TaSe$_3$ – metallic when it is stoichiometric and low defect concentration

The metals tested for fabrication of Ohmic contacts included combinations of thin layers of Cr, Ti, Au, Pd together with a thicker Au layer.

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Electrical Characteristics of Devices with Quasi-1D TaSe$_3$ Channels – Ohmic Contacts

- Current-voltage characteristics of TaSe$_3$ devices with different channel length.

- Linear characteristics at low voltage indicates good Ohmic contact of TaSe$_3$ channel with the metal electrodes.

The contact resistance extracted from TLM data is $2R_C=22 \ \Omega \cdot \mu m$

Current Density in Quasi-1D TaSe$_3$ Nanowires

High-field I-V characteristics showing the breakdown point. In this specific device the breakdown is gradual.

Breakdown current density of about 32 MA/cm$^2$ — an order-of-magnitude higher than that for copper.

Nature of the breakdown — electromigration as established from the low-frequency noise studies.

Resistivity is $2.6 - 6.4 \times 10^{-4}$ Ω-cm.
Current Carrying Capacity of Quasi-1D ZrTe₃ van der Waals Nanoribbons

The breakdown current density, calculated with the AFM measured thickness and SEM measured width, corresponds to \(\sim 10^8\) A/cm², reached at the voltage bias of \(\sim 1.6\) V.

The inset shows low-field I-V characteristics of quasi-1D ZrTe₃ devices with different channel lengths.

Comparison with Copper Interconnects – Model Prediction

Resistivity trend from the Fuchs-Sondheimer model for the electron–nanowire surface scattering and the Mayadas-Shatzkes model for the electron–grain boundary scattering.

Electrical resistivity of Cu nanowires normalized to the bulk resistivity as a function of $W$.

Specularity parameters $p$ defines electron scattering from nanowire surfaces; reflectivity $R$ determines electron scattering from grain boundaries.

Testing Prototype Interconnects Implemented with CVD Grown Quasi-1D Bundles of TaSe$_3$

A.A. Balandin and L. Bartels, SRC – Intel Corporation: Task 2796.001 Fabrication and Testing of Quasi-1D van der Waals Metal Interconnects


One needs to find quasi-1D van der Waals material with low bulk resistivity → UCR – Stanford – NSF DMREF project on computational discovery of 1D materials.

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Polymer Films with Quasi-1D van der Waals Materials

Chemical Exfoliation of CVT Material

→ Polymer composite films containing fillers comprised of quasi-1D van der Waals materials.
→ Fillers can exfoliation into bundles of *atomic threads*.
→ These nanostructures are characterized by extremely large aspect ratios of up to $\sim 10^6$.

Quantum confinement works in different ways in 1D van der Waals materials
Electromagnetic Interference (EMI) Shielding – New Functionality

X-Band frequency range (8.2 GHz – 12.4 GHz)

To determine EMI characteristics, we measured the scattering parameters, $S_{ij}$, using the two-port PNA system.

Extremely High Frequency (EHF) band (220 GHz – 320 GHz)

EMI shielding efficiency was determined from the measured scattering parameters using Agilent N5245A vector network analyzer (VNA) with a pair of frequency extenders.

(a) Shielding effectiveness of pristine epoxy; (b) Reflection, absorption, and total shielding effectiveness.

- Note that absorption is the dominant mechanism in blocking the EM waves in EHF band.
- The films are electrically insulating: local EM coupling to the quasi-1D nanowires

EM-Polarization Selective Composites with Quasi-1D van der Waals Metallic Fillers

Aligned fillers of quasi-1D metals

Quasi-1D materials are building blocks for new functionality

Angular dependency of (a) the reflection, absorption, and total shielding effectiveness, and (b) reflection absorption, and transmission coefficients of sample D with 1.61 vol% aligned quasi-1D TaSe$_3$ fillers. As shown in (b) the reflection is highly correlated with sample orientation whereas absorption varies weakly.

Electronic Devices Printed with Inks of Quasi-1D van der Waals Materials

TiS$_3$ is a semiconductor

Charge Density Waves: Quasi-1D Crystals

Normal state $T > T_c$

Electron Density $\rho_e = \text{const}$

Atomic Spacing $\frac{\hbar}{a}$

Peierls state $T < T_c$

Electron Density $\rho_e = \rho_0 + \rho_1 \cos(qx + \lambda_c)$

Atomic Spacing


Macroscopic quantum phenomena: coherence length > 1 \(\mu\text{m}\)

Quantum materials

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Depinning and Sliding of CDWs in Bulk Quasi-1D CDW Materials

CDWs in metallic crystals form due to the wave nature of electrons – a manifestation of quantum mechanical wave nature of electrons – causing the electronic charge density to become spatially modulated.


For fields larger than a threshold field $E_T$, the sliding CDW provides a second conduction path next to a single-particle electron conduction. Macroscopically this leads to non-linear electrical conductivity and oscillations for large fields.
Other Examples of Current Oscillations in Bulk Quasi-1D CDW Materials

Rebirth of the Field of CDW Materials: Quasi-2D Films of 1T-TaS$_2$

Ambient-pressure phases of 1T-TaS$_2$. The phases are: a metallic phase at temperatures above 550 K; an IC-CDW phase above 350 K; an NC-CDW phase above 190 K; a C-CDW Mott phase below 190 K. Also shown are the Ta atom distortions in the fully commensurate phase and the crystal structure of 1T-TaS$_2$.


There are multiple phase transition points – some of them are above RT.
Two-Terminal CDW Quasi-2D 1T-TaS$_2$ Devices

- NC-CDW -- IC-CDW transition can be induced by changing the temperature or passing electrical current
- Use NC-CDW – IC-CDW transition instead of depinning and sliding
- NOT another resistive switch
The First Room Temperature CDW Device

Idea: utilize NC-CDW–IC-CDW transition at 350 K

A switch that is not a transistor

This is not a resistive switching

CDW device can be low power and fast
The threshold switching effect is prominent from 78 K to 320 K. The blues arrows indicate the voltage sweep direction for the measurement at 78 K. For all the other temperatures, $V_H$ is always higher than $V_L$. The switching is prominent up to 320 K, and becomes less pronounced as the temperature approaches the NC-CDW–IC-CDW transition at 350 K. As shown in the inset, at 345 K (red curve), the switching is still measurable.

Oscillator Based on 1T-TaS$_2$ Device

Circuit schematic of the oscillator consists of the 1T-TaS$_2$ film, a series connected load resistor, and a lumped capacitance from the output node to ground. The load resistance is 1 kΩ.

Voltage oscillations under different $V_{DC}$. The circuit oscillates when $V_{DC}$ is within the range of 3.83-3.95 V. The frequency is 1.77 MHz, 1.85 MHz, and 2 MHz when $V_{DC}$ is 3.83, 3.86 and 3.95 V, respectively.

Different operation mechanism from early devices – no de-pinning

Allows for high T operation

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An Integrated 1T-TaS$_2$ – h-BN – Graphene Oscillator

The SEM image of the integrated 1T-TaS$_2$–BN–graphene voltage controlled oscillator. The graphene and the TaS$_2$ are highlighted by dashed lines.

Output waveforms at different gate biases when $V_{DC}$ is fixed at 3.65 V. The oscillation frequency is tunable with gate biases in the range of 0.68 V to 1.8 V. The different waveforms are vertically offset of 0.25 V for clarity.

The dependence of oscillation frequency as function of gate bias.

Blue circles show the frequency of the oscillation under increased gate bias. The frequency can be adjusted monotonically with the tuning sensitivity of 0.3 MHz/V.

The red squares are the resistance value of the G-FET under different gate biases with fixed $V_{DC}=2.4$V.

1T-TaS$_2$ CDW Devices Under X-Ray Irradiation

TID response of 1T-TaS$_2$ devices up to 1 M rad (SiO$_2$). (a) I-V curves measured after each X-ray irradiation step. (b) Threshold voltages, $V_H$ and $V_L$, threshold currents, $I_H$ and $I_L$ as function of dose. (c) Extracted resistance at the high resistance and low resistance states as a function of dose.

Carrier concentration: $10^{21}$ cm$^{-2}$ - $10^{22}$ cm$^{-2}$

Radiation Hardness of CDW Devices


(a) Circuit schematic diagram of a self-sustaining oscillator implemented with one 1T-TaS$_2$ device and a load resistor.

(a) Oscillation waveform before and after 1 Mrad(SiO$_2$) X-ray irradiation
Proton Bombardment Immune Devices Based on CDW Transition in 1T-TaS$_2$

The quasi-two-dimensional (2D) 1T-TaS$_2$ channels show a remarkable immunity to bombardment with the high-energy 1.8 MeV protons to, at least, the irradiation fluence of $10^{14}$ H$^+$cm$^{-2}$.

Noise Spectroscopy of CDW Transitions

→ Resistance as a function of the applied electric field measured at RT.
→ Noise spectral density as the function of frequency for several values of the electric field, which include the point of transition from the IC-CDW to the normal metallic phase.
→ Noise spectral density, measured at f=10 Hz, as the function of the electric field.

Electric Field vs Self-Heating Mechanism in CDW Devices

Summary of electric field induced phase transitions at different temperatures for 1T-TaS$_2$ devices. The variation in the electric field required to include the phase transitions is due to different device geometries, thickness of the layers in the device structures, and other variations in the device designs.

Can the CDW Switching be Fast Even If It is Induced by Heating?

We studied the switching transition between the nearly commensurate and incommensurate CDW phases in 1T-TaS$_2$ films using pulse measurements and numerical simulations.

A pulse generator creates repetitive current pulses as short as 8 ns. The generated current is then measured by a mixed-signal oscilloscope.

Experimental and Calculated CDW Current-Voltage Characteristics

Experimental (left) and simulated (right) I-V characteristics for (a) 8 ns, (b) 736 ns, (c) 3,335 ns, and (d) 13,333 ns pulses. For the shortest duration shown (8 ns), no hysteresis window is observed. With increasing the pulse duration, the width of the hysteresis window expands and then shrinks again. This behavior is attributed to the transient heat diffusion characteristics of the 1T-TaS$_2$ film, during the up and down sections of the pulse, causing the film to attain different temperatures at fixed bias in the hysteresis region.


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Thermally Driven CDW Switching

- Experimental, and simulated hysteresis window width ($I_c - I_h$) calculated at the constant bias voltage of 1 V as a function of pulse duration. The experimental and theoretical results both follow the same trend, exhibiting a peak at shorter pulse durations and saturating at longer pulse times.

- Our results do not mean that you cannot achieve electrical switching

CDW Switching: Prospects of GHz Switching Speed

We used the experimentally validated model to estimate the device switching speed as the device size decreases. It was found that despite the dominant self-heating effects, tuning of the dimensions can lead to a device that can operate at GHz frequencies.


Experimental and simulated hysteresis window width ($V_C-V_H$) at the constant current of 8 mA and as a function of pulse duration.
The Search for the CDW Depinning and Sliding in Quasi-2D CDW Materials

IV-characteristics of 2D CDW materials are different from those of bulk 1D CDW.


Noise is more sensitive than I-Vs for monitoring CDWs in quasi-2D materials.

In bulk quasi-1D CDW materials, the linear relationship was explained assuming that $f$ is proportional to the CDW drift velocity, $v_D$, so that $f = v_D / \Lambda$, where $\Lambda$ is the characteristic distance.

Since $I_{CDW} = nef \Lambda A$, where $n$ is the charge carrier density, $e$ is the charge of an electron, and $A$ is the cross-sectional area, one obtains: $f = (1/neLA) \times I_{CDW}$

Have We Found the “Narrow Band Noise” in Quasi-2D CDWs?

Frequency, $f_0$ of the noise peaks as a function of the current through 1T-TaS$_2$ device channel. The inset shows a microscopy image of a representative 1T-TaS$_2$ device structure with several metal contacts.

Relation between the COW current and fundamental oscillation frequency in NbSe$_3$. The inset shows $I_{\text{CDW}}/f_0$ vs. temperature. After Bardeen et al. (1982).
The Current Oscillations are due to Hysteresis at the NC-CDW – IC-CDW Transition

I-Vs of tested 1T-TaS$_2$ device which revealed “narrow band noise”. The hysteresis loop at the bias voltage $V = 0.9$ V corresponds to the transition from the NC-CDW phase to the IC-CDW phase induced the applied electric field.

The current oscillations appear to be similar to our earlier result – this is not the “narrow band noise.”
Current-voltage characteristic of the 1T-TaS$_2$ devices on Si/SiO$_2$ substrate at room temperature. The direction of the current sweep is indicated with the arrows. The data are presented for two devices with different channel length fabricated on the same structure. The arrows indicate the direction of the current sweep.
Derivatives of the I-V Characteristics

(a) The current in the forward (red) and reverse (blue) sweeping overlaps. The straight black line is shown for comparison. No deviations from the non-linearity are observed in this bias range. (b) The derivative of current-voltage characteristics revealing a strong change in the electron transport.

The threshold in 2D is ~1 kV/cm while in 1D systems it is ~ 40 mV/cm – 4 V/cm
Noise Spectroscopy Reveals the Depinning in 2D 1T-TaS$_2$ CDW Devices

Likely Signatures of Sliding CDWs in 2D Materials

(a) Normalized noise spectral density multiplied by the frequency, $S_n/I^2 \times f$, as a function of frequency at different applied bias voltages. (b) The noise amplitude as a function of the bias voltage. Note the break in the y-axis. The noise level experiences a drastic increase at the depinning point. The inset shows the dependence of the corner frequencies with the current in the device channel. 

→ Extremely small contribution of CDW current to the total current in 2D systems
→ Quasi-1D van der Waals materials are as interesting as quasi-2D van der Waals materials

→ Going from quasi-2D to quasi-1D brings a lot of new functionalities and potential applications

→ The charge-density-wave quantum materials and devices field is in a rapid growth mode

→ The rebirth of the CDW field is to a large degree due to going from quasi-1D to quasi-2D van der Waals materials

Acknowledgements
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