Two-Dimensional van der Waals Heterostructures for Quantum Transport and Ultrafast Optoelectronics

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Graphene

One atomic thick carbon film.

First 2D material in human history.

2D = Graphene

3D = Graphite



Discover of Graphene





Andre Geim

Konstntin Novoselov

Two-dimensional atomic crystals

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Edited by T. Maurice Rice, Swiss Federal Institute of Technology, Zurich, Switzerland, and approved June 7, 2005 (received for review April 6, 2005)

We report free-standing atomic crystals that are strictly 2D and can be viewed as individual atomic planes pulled out of bulk crystals or as unrolled single-wall nanotubes. By using micromechanical cleavage, we have prepared and studied a variety of 2D crystals including single layers of boron nitride, graphite, several dichalcogenides, and complex oxides. These atomically thin sheets (essentially gigantic 2D molecules unprotected from the immediate environment) are stable under ambient conditions, exhibit high crystal quality, and are continuous on a macroscopic scale.

graphene | layered material

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wafer (Fig. 1*d*), because even a monolayer adds up sufficiently to the optical path of reflected light so that the interference color changes with respect to the one of an empty substrate (phase contrast). The whole procedure takes literally half an hour to implement and identify probable 2D crystallites. Their further analysis was done by atomic force microscopy (AFM), for which single-layer crystals were selected as those exhibiting an apparent (12) thickness of approximately the interlayer distance in the corresponding 3D crystals.

Despite its simplicity, the described cleavage technique has several nonobvious features that are instructive to analyze,





Layered Material



Discover of Graphene



The Nobel Prize in Physics 2010

"for groundbreaking experiments regarding the two-dimensional material graphene"





Andre Geim

Konstntin Noveselov

Graphene: Dirac Particles in 2D



Room Temperature Quantum Hall Effect

T= 300 K, High magnetic field

Landau level splitting





K.S. Novoselov et al, Science 315, 1379 (2007)

Graphene Mobility



Graphene on SiO₂ mobility (<20,000 cm²/V.s) is smaller than theoretical expectation. Material intrinsic disorder or extrinsic effect?

Graphene Mobility



Problem: 3D substrates are not a good match for 2D materials! (Disorder, Scattering, Doping...)

Suspended Graphene

Toward high moblity device



HF etching -> critical pointing drying



AFM image of suspended graphene



You should not apply to high gate voltage, otherwise...

Collapsed graphene devices...





Hexagonal Boron Nitride



Comparison of h-BN and SiO₂

	Band Gap	Dielectric Constant	Optical Phonon Energy	Structure
BN	5.5 eV	~4	>150 meV	Layered crystal
SiO2	8.9 eV	3.9	59 meV	Amorphous

- < 2% lattice mismatch to graphene
- atomically flat

- chemically inert, stable to high temp.
- no dangling bonds- good dielectric properties



Polymer Transfer of Graphene onto hBN



C.R. Dean

Making Layered Structures



The reality...



Motivation for Edge Contact



K. Nagashio, et al IEDM. 2009

"Metal/Graphene Contact as a Performance Killer of Ultra-high Mobility Graphene"



J.A. Robinson, et al APL. 2011











Van der Waals Assembly



Ultraclean technique – graphene never exposed to polymer

Edge Contacts



Graphene Quantum Transport



Negative refraction and Veselago lens (Electro-Optics)





Beyond Graphene



Semi metal: Graphene, ... Insulator: hBN, ... Semiconductor: MoS_2 , $MoSe_2$, WSe_2 , WS_2 , ... Superconductor: NbSe_2, Bi_2Sr_2CaCu_2O_{8-x}, ZrNCI ... Complex-metallic compound: TaS_2 , $TaSe_2$, ...



F. Xia et al., Nature Photonics 8, 899 (2014)

van der Waals Heterostructure

2D building block





LED

Advanced technology



Van der Waals Heterostructure







Memory



Tunneling Diode



Solar cell



Transition Metal Dichalcogenides (TMDCs)



M. Chhowalla et al, Nature Chemistry (2013)



K. Kalantar-zade et al, Advanced Funct. Mat. (2015)

- Semiconductor MoS₂, MoSe₂, WS₂, WSe₂, etc (Bandgap 1 ~ 2.5 eV, N/P-type)
- Superconductor: NbSe₂, NbS₂
- Charge density wave: TaS₂
- Topological materials: MoTe₂, WTe₂ New physics at 2D limit

2D Semiconductor



Monolayer TMDC: MoS₂

Broken inversion symmetry



Valley degree of freedom and Berry curvature

Strong spin-orbit coupling



Valley dependent optical selection rule



K. F. Mak et al, Nature Nanotechnology (2013)

Optical absorption spectra





 $\Delta_{SO} \sim 150 \text{ meV} (MoS_2)$ ~ 400 meV (WSe₂)

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- 1. High mobility?
- 2. Low contact resistance?

TMDC Electrical Properties



- Direct bandgap at monolayer (1.8 ~ 2.0 eV)
- High on/off ratio (~ 10⁸)
- High mobility (1 ~ 100 cm²/Vs at RT)
- Piezoelectricity



B. Radisavljevic et al., Nature Nanotech. 6, 147 (2011)

TMDC Electrical Properties (mobility)





- 2D materials are extremely sensitive extrinsic effect.
- Intrinsic limit acoustic and optical phonon
- Charged impurity scattering dominant at LT.
- Surface roughness of substrate
- Contact resistance dominant.

Contact Issue













- TMDC performance limited by contact
- Finite Schottky barrier (TMDC/Metal interface)
- 1T-phase engineering (Decrease of contact resistance)
- Graphene electrode (Ohmic contact at LT)

Graphene/MoS₂ Contact



Barrier free contact at MoS2/Graphene interface



Ohmic contact at low temperature

Large tunable of Fermi every of graphene

Co Contact with Monolayer hBN



Ohmic contact with monolayer hBN layers.



Approaching to low carrier density regime.

Via contact to 2D Material



MoS₂ Heterostructure





X. Cui, G.H. Lee, Y.D. Kim et al, Nature Nanotech. (2015)

Ultraclean van der Waals interface Universal platform for 2D material

MoS₂ Heterostructure

Record high mobility in MoS₂



 $\sigma = ne\mu_{Hall}$, where *n* is carrier density

Hall mobility of $MoS_2 = 1,000 \sim 30,000 \text{ cm}^2/\text{Vs}$ Reduce the charged impurity densities by clean interface

First observation of quantum oscillation from monolayer MoS₂



Quantum mobility $\mu_Q \simeq 1,400 \text{ cm}^2/\text{Vs}$ (one set oscillation 6.7 T)

 $\mu_Q = 1 / B_q$

Landau fan diagram and periodicity changed by gate voltage

Anomalous quantum plateau: Valley and spin Zeeman effect?

Y.D. Kim *et al*, in preparation

Valley and spin Zeeman effect

Valley and spin polarization under magnetic field

Spin Zeeman effect: $2S_z \mu_B B$ Valley Zeeman effect: $\alpha \tau_z \mu_B B$

where $\mu_B = \frac{e\hbar}{2me_e} = 0.05$ meV/T is Bohr magneton , $\alpha = m_0/m^*$, and m^* is the effective mass.

Observation of coupled valley-spin Zeeman effect

Peak splitting at high carrier density Smearing of peak splitting at high Temp.

Effective mass ~ 0.49 m_o

Spin sub-band crossover

Quantum scattering time: From Ando formula and Dingle term $\tau_Q \rightarrow \frac{\Delta \rho_{xx}}{\rho_0} = 4\gamma_{th} \exp(-\frac{\pi}{\omega_c \tau_Q}),$ where $\gamma_{th} = \alpha / \sinh(\alpha), \alpha = 2\pi^2 k_B T / \hbar \omega_c$ Open extra scattering pathway:

Band cross point: $n_F \sim 9.5 \times 10^{12} \ cm^{-2}$

Conduction band spin splitting Δ_{so} = ~ 10 meV

TMDC Metal

•NbSe₂, NbS₂, TaS₂, TaSe₂

•High electronic density

•Electronic instability (Charge density wave, Superconductivity, Magnetism)

Air sensitive van der Waals Materials

	Graphene family	Graphene	hBN 'white graphene'			BCN	Fluorograph	ene	Graphene oxide
	2D chalcogenIdes	MoS ₂ , WS ₂ , MoSe ₂ , WSe ₂		Semiconducting dichalcogenides:		$\begin{array}{c} \mbox{Metallic dichalcogenides:} \\ \mbox{NbSe}_2, \mbox{NbS}_2, \mbox{TaS}_2, \mbox{TiS}_2, \mbox{NiSe}_2 \mbox{ and so on} \end{array}$			
				MoTe S ₂ , ZrS	e_2 , WTe ₂ , e_2 and so on	Layered semiconductors: GaSe, GaTe, InSe, Bi ₂ Se ₃ and so on			
2D oxides		Micas, BSCCO	MoO ₃ , WO ₃			Perovskite-type: LaNb ₂ O ₇ , (Ca,Sr) ₂ Nb ₃ O ₁₀ , $Bi_4Ti_3O_{12}$, Ca ₂ Ta ₂ TiO ₁₀ and so on		Ni(Oł	Hydroxides: H) ₂ , Eu(OH) ₂ and so on
	2D oxides	Layered Cu oxides	TiO ₂ , MnO ₂ TaO ₃ , RuO ₂ ar	$D_2, V_2O_5,$ and so on					Others

Semiconductor: Black phosphorous **Superconductor**: NbSe₂, NbS₂, FeSe High Tc superconductor: BSCCO **Charge density wave**: TaS₂, NbSe₂ **Topological material**: MoTe₂, WTe₂ Ferromagnetic: CrSiT₃ **Magnetic insulator**: EuS₂

Surface oxidation alter intrinsic properties at 2D limit!

Automatic system

Home-built automatic, exfoliation, searching and stacking

Allow efficient and systematic study at intrinsic limit!

Hard work

Manually search and stack

Charge Density Wave

Modulated electron density (charge density wave)

Charge Density Wave in IT-TaS₂

No CDW wave at 2D limit!

Charge Density Wave in IT-TaS₂

Modulation of electron density by distortion of ion lattice. Transport Electron diffraction from TEM

Oxide on TaS2 (Stack in air) Phase transition suppressed by disorder

Charge Density Wave in TaS₂

TaS2 Heterostructure Atomically thin CDW at clean limit

Clear CDW at 2 nm

CDW in 2D limit: increase barrier height

Superconductivity

Zero resistance

Meissner effect

1911: K. Onnes discover superconductor

What is nature of intermediate metallic phase? New quantum metallic phase (Bose metal)?

2D Superconductor

NbSe₂: Single crystalline type II superconductor

Atomically thin NbSe₂

Superconducting or insulating transition only? Surface oxidation layer alter electronics properties?

NbSe₂ heterostructure

Zero-resistance superconducting transition Real 2D superconductor!

Pauli paramagnetism limit

 $\mu_B H_P \sim |\Delta|$

$$H_P = \frac{4T_c}{\pi\mu_B} = 1.84T_c \sim 9.5 \text{ T}$$

$$\mu_{\parallel} \sim \frac{H}{H_0} \mu_B$$
$$\mu_B \quad \frac{H^2}{H_0} \sim |\Delta|$$
$$H_{c2} \sim \sqrt{H_{so}H_p} \sim 50 \ T \gg H_p$$

Van Vleck paramagnetism

- In-plane critical field: > 20 T

- Larger than Pauli paramagnetic limit of 9.58 T

 $-2\Delta_{so} = 80 \text{ meV}, H_{so} = 700 \text{ T}$

2D Superconductor

- Clear metallic transition
- No insulating transition
- Large phase fluctuation not kill

Cooper pair number fluctuation

Nature of quantum metallic phase (Bose metal)?

Ultrafast Optoelectronics

Large Scale Graphene Image Sensor

ARTICLES

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photonics

Broadband image sensor array based on graphene-CMOS integration

Stijn Goossens¹⁷, Gabriele Navickaite¹¹, Carles Monasterio¹¹, Shuchi Gupta¹¹, Juan José Piqueras¹, Raúl Pérez¹, Gregory Burwell¹, Ivan Nikitskiy¹, Tania Lasanta¹, Teresa Galán¹, Eric Puma¹, Alba Centeno², Amaia Pesquera², Amaia Zurutuza², Gerasimos Konstantatos^{1,3*} and Frank Koppens^{1,3*}

Light Emission from Graphene ?

Graphene

•Zero-bandgap

•Klein tunneling (No rectification in p-n junction)

Ultrafast energy relaxation
Electron-electron: ~ 10 fs
Electron - optical phonon: 10 ~ 100 fs
Optical phonon decay to acoustic phonon: ~ 1 ps

Non-efficient radiative electron-hole recombination

Incandescence

Light bulb

UV VISIBLE INFRARED 14 5000 K Spectral radiance (kW · sr⁻¹ · m⁻² · nm⁻¹) 12 Classical theory (5000 K) 10 8 6 4000 K 4 2 3000 K 0 0 0.5 1.5 2.5 1 2 3 Wavelength (µm)

 $I = \frac{2hc^2}{\lambda^5} (\exp \frac{hc}{\lambda k_B T} - 1)$

T : electron temperature

Blackbody radiation

Hot Electrons Luminescence in Graphene

Superior properties of graphene

Ideal material for thermal radiation

Excitation Hot electron cooling pathway in Graphene T_E T_E T_OP Optical phonon Relaxation Bottleneck T_AP Acoustic phonon

Ambient

Planck's law $I(\omega) \sim 1/(\exp(\hbar\omega/k_B T_e) - 1)$

•Very weak electron-acoustic phonon coupling.

•Non-equilibrium phonon mode.

•Non-equilibrium temperature of graphene $T_E \sim T_{OP} > T_{AP}$

Efficient thermal radiation source

Graphene on Substrate

M.-H Bae et al, Nano Lett. (2010)

M. Freitag et al, Nature Nanotech. (2010)

- •Graphene under high bias.
- •Thermal radiation at near IR emission.
- •Follow Planck's law (T < 600 K). $I(\omega) \sim \omega^3 / (\exp(\hbar\omega/k_B T) - 1)$
- •Low radiation efficiency (~10⁻⁶)
- Dominant heat dissipation by substrate
- Strong electron scattering (charged impurity, defects of substrate)

Performance of graphene light emitters are limited by substrate.

Suspended Graphene

Y. D. Kim et al, Nature Nanotech. (2015)

- Minimize the substrate effect
- Reduce vertical heat dissipation to substrate
- Approaching to the intrinsic characteristic

Bright Visible Light Emission from Graphene

Vsd = 2.4V -> 2.9V -> 2.4V

Electric pulsed |Vsd| = 7.5 V -> 8 V

Hexagonal Boron Nitride (hBN)


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Comparison of h-BN and SiO<sub>2</sub>
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	Band Gap	Dielectric Constant	Optical Phonon Energy	Structure
BN	5.5 eV	~4	>150 meV	Layered crystal
SiO2	8.9 eV	3.9	59 meV	Amorphous

- •Single-crystal, atomically flat, no defect.
- •High optical phonon energy.
- •Ideal dielectric material for 2D material.

van der Waals Heterostructure

At limit of acoustic phonon scattering. Intrinsic transport-suppress electron scattering

Ultrafast Graphene Light Emitter

hBN/Gr/hBN heterostructure

- •Bright visible light emission
- •Electron scattering suppress is more dominant
- •hBN encapsulation for practical light source even in ambient condition
- •Life-time above 4 year

Tailoring Thermal Radiation of Graphene

Black body thermal radiation

 $I(\omega, T) = E(\omega)n(\omega, T)D(\omega)$

 $E(\omega)$: Mode energy, $n(\omega, T)$: photon occupation $D(\omega)$: Local optical density

•Strong light-matter interaction of graphene

•Engineering local optical density in sub-wavelength

•Easy to integration to arbitrary structures

Optical cavity mode

Y.D. Kim et al, Nano Letters (2018).

Ultrafast Graphene Light Emitter

GHz bandwidth graphene light emitter

Hyperbolic plasmon-phonon polariton

•Electrically driven GHz range thermal radiation source

- •10 GHz bandwidth (FWHM ~ 92 ps)
- •Thermal relaxation time $\tau = C_e/\Gamma$ (heat capacity of graphene and hot electron cooling rate) – Significant heating of 3 nm hBN layers at interface •Direct and efficient electron cooling pathway by graphene/hBN interface -Intrinsic thermal radiation modulation speed above 100 GHz

Large Scale Graphene Light Emitter

Hyung-sik Kim Ken Shepard group/ Samsung Display

- Scale up using large scale CVD graphene
- Over 60,000 graphene light emitter array on chip
- PECVD graphene No need transfer process
- CMOS technology compatibility

2D Semiconductor

Transition Metal Dichalcogenides

Intrinsic Band gap - High on/off ratio

Direct band gap - Photoluminescence

2D Semiconductor Lateral LED

Lateral P-N junction

J. S. Ross et al., Nature Nanotech. (2015)

B. W. H. Baugher et al., Nature Nanotech. (2015)

- Atomically thin LED from WSe₂, MoS₂, WS₂. etc
- Formation lateral P-N junction by split gate
- Light emission from P-N junction interface
- EQE: ~ 0.2 % limited by contact resistance

2D Semiconductor Vertical LED

Vertical tunneling structure

<sup>Gr/hBN/WSe₂/hBN/Gr vertical heterostructure
Coincide the EL and PL at 1.65 eV
Direct electron and hole injection via tunneling
EQE: 1~8 %
Helicity light emission is possible</sup>

Y.D. Kim et al, in preparation and demonstrated by Manchester group

Beyond LED

Valleytronics LED

Valley polarized LED

2D ferromagnetic/TMDC heterostructure

Exciton-Polariton BEC

Polariton

Strong light matter interaction Exciton-Photon (Bosonic)

Polariton Laser

Ultra-low threshold lasing

Quantum Emitter at Room Temperature

2D single photon source

4.11 eV

T. T. Tran et al, Nature Nanotech. (2016)

Single photon source at room temperature

Developing electrically driven single photon source Potential for optical quantum information process

Thank you very much!

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