Two Dimensional Material, Their Properties, Application and Manufacturing

Reading Assignment

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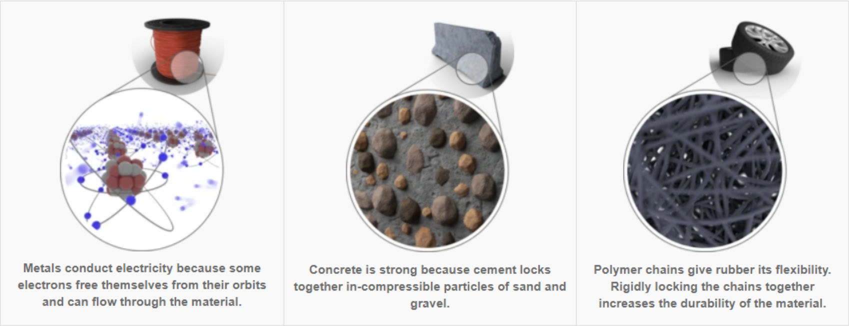
Outline

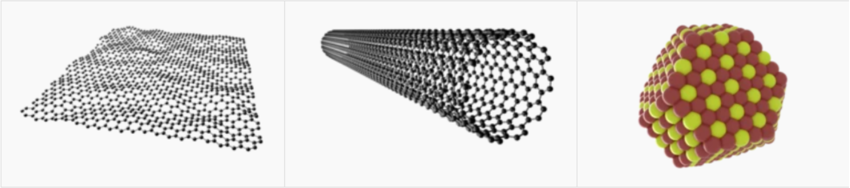
Foundation of Technology

- How well we understand material system
- Material properties depends on what it is made up
- Does the properties depend on size?



Nanomaterials

- Having at least one dimension in nano-scale ($< 100nm$)
- Materials -
  - $0D$ Material - nanoparticle, e.g. quantum dots
  - $1D$ Material - nanotube/nanowire, e.g. carbon nanotube
  - $2D$ Material - sheet or film with thickness in nano-scale, e.g. graphene
  - $3D$ Material or Bulk material - e.g. block of iron.

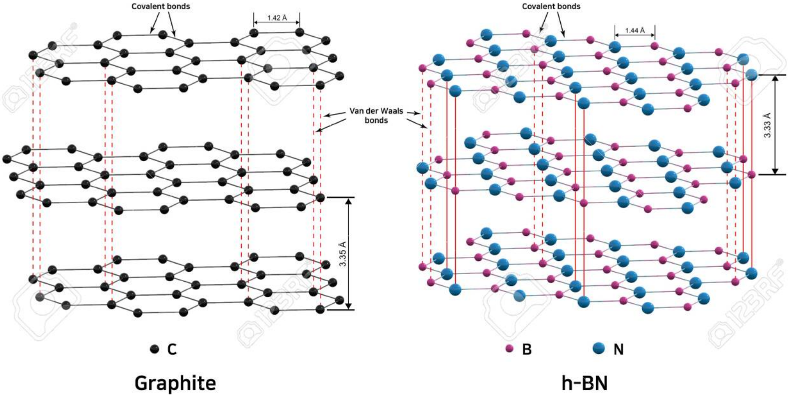


Properties and example of 2D Material

- Due to nanoscale dimension following properties are affected.
  - Electrical and thermal conductivity
  - Chemical reactivity
  - Mechanical properties
  - Interaction with light and other radiation and beam of particle
  - New phenomenon - Quantum hall effect, Berry phase

- Example - Graphene, Hexagonal Boron Nitride (h-BN), Transition Metal Di-Chalcogenides(TMDCs), Phosphorene, Xenes etc.

Graphene and h-BN

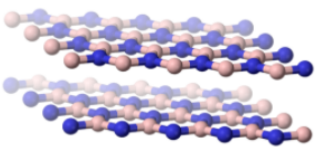


Graphene

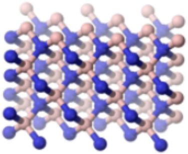
- Covalently bonded hexagonal lattice of carbon
- One atom thick - $0.14nm$
- Semimetal - Valance and conduction band touch each other
- Unique band structure - Extremely high speed of electron($\frac{1}{300}$ the speed of light) leading to exceptional thermal conductivity
- Has highest tensile strength
- Fascinating Physical phenomenon - Quantum hall effect, Berry phase

h-BN

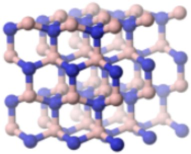
- Has same crystallographic appearance as graphene except that it has B and N atom
- Wide band gap insulator



Hexagonal form (h-BN)
hexagonal analogous to graphite



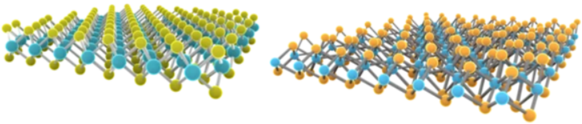
Cubic form (c-BN)
sphalerite structure
analogous to diamond



Wurtzite form (w-BN)
wurtzite structure
analogous to
lonsdaleite

Transition Metal Dichalcogenides or TMDCs or MX_2

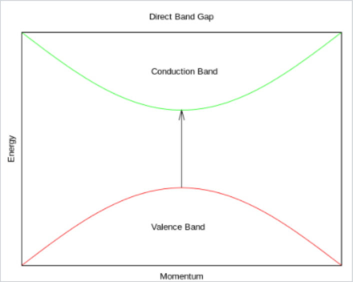
- M - Metal atom, e.g. Mo, W
- X - Chalcogens/oxygen family, e.g. S, Se, Te
- van der Waals material - layer material
- Metal layer is sandwiched between chalcogenide layer
- Two phases - 2H phase (triagonal, semiconductor, e.g. MoS_2, WS_2, $MoSe_2$) and 1T phase (hexagonal, metallic, e.g. WTe_2)



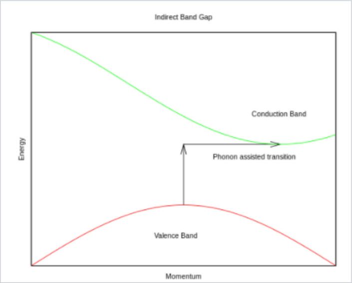
Left: Molybdenum disulphide (MoS_2). Right: Tungsten ditelluride (WTe_2). Both are 2-dimensional transition metal dichalcogenides. MoS_2 is most commonly found in the semiconducting 2H phase, while WTe_2 prefers to adopt the metallic 1T phase.

Direct and Indirect Band gap

- 2H phase - indirect band gap in bulk and direct band gap in monolayer - suitable for optoelectronics
- Direct and Indirect band gap



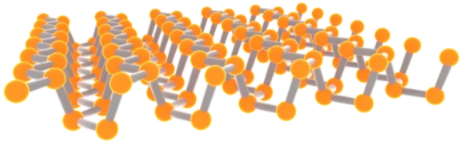
Energy vs. crystal momentum for a semiconductor with a direct band gap, showing that an electron can shift from the highest-energy state in the valence band (red) to the lowest-energy state in the conduction band (green) without a change in crystal momentum. Depicted is a transition in which a photon excites an electron from the valence band to the conduction band.



Energy vs. crystal momentum for a semiconductor with an indirect band gap, showing that an electron cannot shift from the highest-energy state in the valence band (red) to the lowest-energy state in the conduction band (green) without a change in momentum. Here, almost all of the energy comes from a photon (vertical arrow), while almost all of the momentum comes from a phonon (horizontal arrow).

Phosphorene

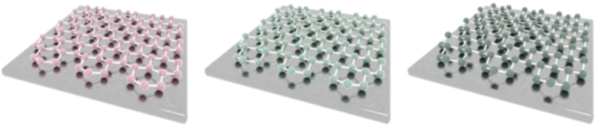
- Direct band gap semiconductor
- Wrinkled honey comb structure
- Band gap - tunable by stacking layers
- Good charge mobility - about $1000 \frac{cm^2}{Vs}$
- Anisotropic
- Application - Optoelectronics and transistors



Phosphorene (also known as 2D black phosphorus) is a 2D semiconductor that is a promising material for transistors.

Xenes

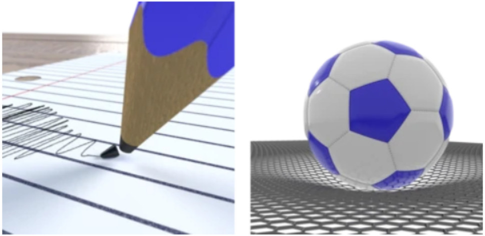
- Monolayer of silicon(silicene), germanium(germanene), tin(stanene)
- Buckled hexagonal structure
- Can not be exfoliated, only grown epitaxially on substrate
- Have strong interaction with the substrate
- Recent - antimonene, bismuthine (magneto-electronics)
- Potential Application - Field Effect Transistors, topological insulator



Silicene (left), germanene (middle) and stanene (right) have buckled hexagonal structure.

Why are 2D material different from bulk materials?

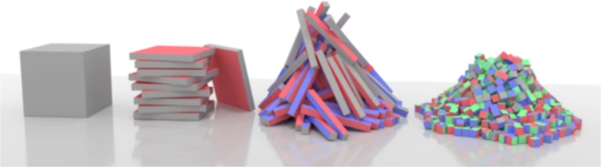
- Removal of van der Waal interaction



Graphite (left) can be easily broken because of its weak interplane Van der Waals forces, while graphene (right) has only covalent bonds and so it extremely strong - a monolayer is strong enough to support a football.

Why are 2D material different from bulk materials?

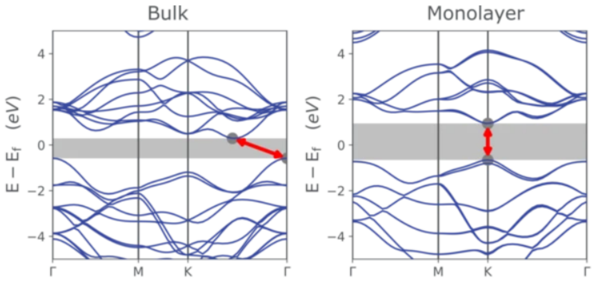
- An increase in ratio of surface area to volume
  - 2D material are more reactive than their bulk counterpart
  - Suitable for sensing application



When an object is divided into smaller components, its total surface area increases. From left to right: a bulk object is divided into 2D sheets - exposing the red surfaces, and the sheets are divided into 1D rods - further exposing the blue surfaces. Finally, the rods are divided into dots - exposing additional green surfaces.

Why are 2D material different from bulk materials?

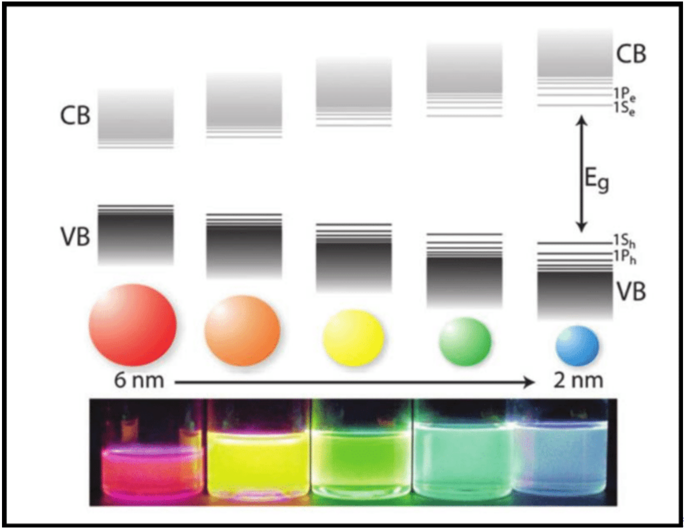
- Confinement of electrons in a plane
  - Change in band structure - Indirect to direct
  - Increase in band gap - Q. Why does the conductivity increases in case of graphene but not in case of h-BN?



Band structure diagram of (left) bulk and (right) monolayer MoS_2 showing the crossover from indirect to direct bandgap accompanied by a widening of the bandgap.

Quantum Confinement

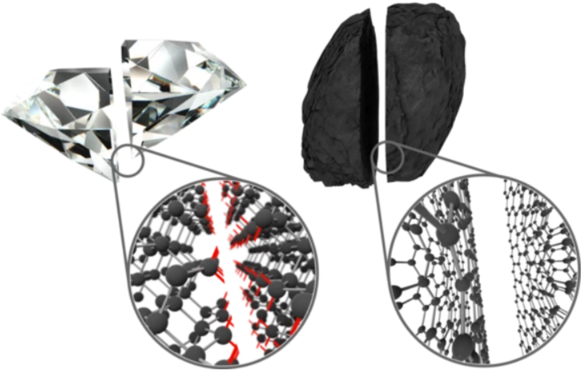
- Increase in band gap
- Bohr radius



Making of 2D Materials

- Graphene - First 2D material, 2004, Scotch-tap mechanical exfoliation
- van der Waals Material - Layered material
- Two approaches
  - Top-down Approach - Start with bulk material make it thinner, e.g. Mechanical exfoliation, Liquid exfoliation
  - Bottom-up Approach - Start with atomic ingredients and assemble them together, e.g. Chemical Vapour Deposition, Solution based chemical synthesis

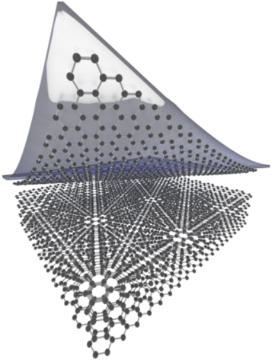
Top-down Approach



Each carbon atom in diamond (left) has bonds extending in 3 dimensions - meaning that when diamond is cut in any orientation, some of these bonds must be broken and are left 'dangling' (shown in red). The atoms in graphite (right) have bonds extending in only 2 dimensions, so when it is cut in an orientation parallel to the bonds, none of them are broken.

Mechanical Exfoliation or Scotch Tap Method

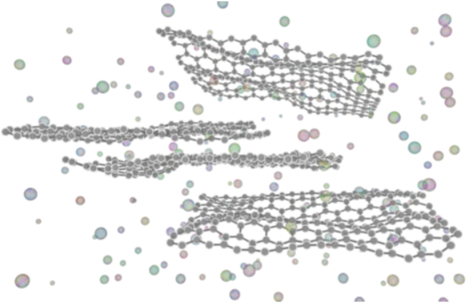
- Monolayer yield is low
- No control of size and shape
- Size - reasonable - few microns to 100 microns
- Quality - excellent
- Popular for van der Waals material and lab based studies



Mechanical exfoliation involves peeling successive layers from a Van der Waals material using a tape.

Liquid Exfoliation

- Use of organic solvent to create force between layer
- Sonication, Use of reactive ions
- Highly scalable
- Low monolayer yield, small flake size ($< 100nm$)
- Not suitable for optoelectronic application - high density of defects, residual solvent



Liquid exfoliation often uses bubbles to force layers apart.

Chemical Vapour Deposition (CVD)

- One or more precursor gases (containing ingredients for the film) are passed through a heated chamber where they react with each other or with the substrate to form thin layer of required material.
- Successfully applied - Graphene, TMDCs
- Complex and expensive
- Highly scalable and quality approaches that of mechanical exfoliation
- Similar bottom up approaches - Physical Vapour Deposition (PVD), Vapour Phase Transport (VPT), Molecular Assembly, Atomic Layer Deposition

Application of 2D materials

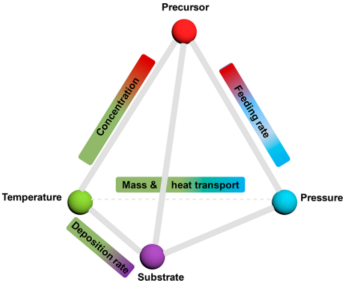
- Transistors and sensors
- Photodetectors
- Battery electrodes
- Topological insulators
- Valleytronics

2D Materials and Their Heterostructures

- Extensive research - tunability, exotic properties of heterostructure
- Need - Method to produce scalable 2D materials and their heterostructure of high quality and low cost
- High Quality - Large area continuous 2D materials with uniform properties with low defect and less grain boundaries
- Example of suitable method - Chemical Vapour Deposition

Material Properties and CVD Parameters

- Materials Features - Size of film, number of layers, morphology, orientation, phases, doping, defects, grain boundaries
- CVD Parameters - Temperature of the source zone and reactor zone, Chamber pressure, Carrier gas flow rate, partial pressure of source material in precursor gas, source substrate distance etc.



CVD Parameters and their effect on Materials Properties

- Precursor
- Temperature
- Substrate
- Pressure
- Modified CVD – PECVD, ICP-CVD

Precursor

- Reactant for CVD Process and Carrier gas
- Control the flow rate and partial pressure
- For Silicon growth
  - Vapour Source - SiH_4 or SiH_2Cl_2 gas (High Purity)
  - Carrier Gas - H_2 and Ar - H_2 terminates the dangling/broken bonds
- For Graphen Growth
  - Source Gas - CH_4
  - Carrier Gas - H_2
  - For Doping - NH_3 or PH_3
- For TMDCs growth
  - Metal Source - Transition metal oxides (MoO_3, WO_3), Transition metal chlorides ($MoCl_5$), Metal foils
  - Chalcogen source - S or Se powders

Precursor

- Problem - Very accurate temperature control in source zone - because vapour pressure of solid material is very sensitive to temperature
- Technology for TMDCs growth - Challenging, less mature
- Improved uniformity of TMDCs - $Mo(CO)_6$, $CS(CH_3)_2$ and H_2S

Temperature

- Affect - flow of carrier gas, chemical reactions of precursors in the gas, deposition rate of product on the substrate
- Determines composition and uniformity of product
- High quality - High Temperature - High cost (Energy) - limited suitable substrate
- High Temperature - Enhances the mass transport, reaction rate and deposition rate.
- For TMDCs growth - Precise control of Temperature in source zone

Temperature

- Two type of growth mechanisms of TMDCs
  - Growth Controlled by chemical reaction rate - high temperature - high precursor concentration, high mass transport
  - Mass transport limited growth mechanism - Low temperature - low precursor concentration, low mass transport
- Gradient of precursor near substrate - Control is difficult
- Nucleation at vapour solid interface
  - high temperature - Thermodynamic process
  - low temperature - Kinetic process
- For MoS_2, at $T > 800^{\circ} C$ - nucleation at the top of bottom layer - Control of number of layers
- High temperature - high growth rate - bigger size

Substrate

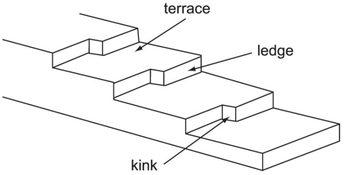
- Substance over which 2D material nucleates and grows
- What makes a material good substrate for a particular 2D material growth?
- Multilayer and monolayer graphene growth - Catalytic active nickel and copper substrate - catalyst and substrate - reason - different carbon solubilities and catalytic activities
- TMDCs growth - intert Si/SiO_2, mica and polyimide, gold or tungsten foil
- Nucleation and growth promoter of TMDCs - PTAS, PTCDA, rGO
- Additives to promote growth of TMDCs - alkali metal halides (NaCl, KI, KCl, NaBr, sodium cholate($C_{24}H_{39}NaO_5$, NaOH)

Substrate

- Growth promoter
  - react with precursor (WO_3, MoO_3) to form volatile intermediate
  - increase the domain size
  - broaden the growth window (??)
  - Opportunities - Function/mechanism are not clear.
- Metal foil substrate
  - gold crystallography - nucleation, domain size - reason - facet dependent binding energy between TMDCs and substrate
  - Orentation - morphology e.g. MoS_2 continuous film of domain size $20\ \mu m$ - vertical orientation - uniformity of precursur improved

Substrate

- Sapphire substrate
  - α-Al_2O_3 with trace amount of Fe, Ti, Cr, V or Mg
  - c-plane - specific orientation and atomically smooth surface terrace
  - TMDCs grown - specific orientation - crystal symmetry and surface terrace of substrate



Pressure

- Varies from few atmospher to several millitor
- Influences gas flow behaviour e.g. at low pressure and same molar flow - high velocity of gas, high volume flow, precursor concentration decreased ($PV = nRT$) - reaction more controllable (How?)
- low pressure CVD - Growth of wafer-scale continuous TMDC film
- Example - MoS_2 growth - partial pressure of $Mo(CO)_6$ is vital
  - low pressure - nucleation only at grain boundaries
  - high pressure - nucleation at the top of first layer (Multilayer product)

Other Parameters of CVD

- Thermal CVD - Thermal energy break the chemical bond of precursor molecule
- Other source of energy - plasma, light, laser - Modified CVD
- PECVD - Plasma Enhanced CVD
  - Can conduct CVD of material for which Thermal CVD is not feasible
  - Plasma - any gas where atoms or molecules are ionized into negatively charged electrons, positively charged ions and neutral species
  - High energy of electrons - break precursor
  - Interaction of surface and energetic ions - increase density of deposited film, remove contaminants, improve quality of film (How?)
  - Example – Conventional – graphen on metal foil at $1000^\circ C$, Now graphene on glass without catalyst at $400 - 600^\circ C$ by PECVD
  - PECVD MoS_2 film – precursor – Mo thin film and H_2S gas at $150 - 200^\circ C$

Other Parameters of CVD

- ICP-CVD – Inductively Coupled CVD
  - Develop novel structure TMDC material e.g. strip S layer of as grown MoS_2 – hydrogenation to get MoSH – thermal seleniztion – MoSSe monolayer TMDC
- Advanced CVD – PECVD, ICP-CVD – create new material, easier making of 2D material

CVD Growth of Single Crystal 2D Materials

- For Practical Application – improve reproducibility of growth process – deep understanding of growth mechanism – link between 2D material growth and CVD process parameters
- Why do we need single crystal material?
  - to investigate the fundamental of nucleation and growth mechanisms
  - to develop approaches for controlling the properties
  - for many practical application large single crystals are needed

Theory of 2D Materials Growth by CVD

- TMDC growth process - evaporation and reduction of metal oxide to suboxide, reaction of suboxide with chalcogen vapours to form TMDC on substrate
- Temperature, gas flow rate, pressure, type of substrate – effect on nucleation and growth
- Different models of nucleation and growth
  - LBL - layer-by-layer growth model
  - LOL - layer-over-layer growth model
  - SDD - screw dislocation driven growth model
  - dendritic growth model
- Which model – degree of supersaturation of reactants

LBL and SDD Growth Model

- LBL Growth model
  - 2D graphene and TMDC growth process
  - Nucleation of new layer has high energy barrier (Why?)
  - High supersaturation – to initiate nucleation and enable reasonable crystal growth
  - Good control of precursor concentration – control the number of layer and well-stacked vertical heterostructures
- SDD Growth Model
  - Reported in solvent synthesis of one dimensional oxides, hydrides and nitrides
  - 2D materials growth at low supersaturation
  - Pyramid like morphologies – new layer initiates at the center of bottom layer and grows not bigger than the bottom layer
  - Provides way to control the number of layer and the stacking rotation

Controlled Growth of Single Crystal 2D Materials

- Seven features of 2D Material we would like to control

Grain Size

- Small grain – more grain boundaries
- Grain boundaries – worsen electronic, mechanical and thermal properties – reason – scattering of carriers, introducing more defects
- Practical Application – Large area 2D materials – large grain size
- Requirements – Effective methods to grow large single crystal 2D TMDCs
- Currently – submicrometer to centimeter scale 2D Materials – MoS_2, WS_2, WSe_2, $MoTe_2$
- Strategies to increase grain size - Two
  - Decrease nucleation density
  - Maintain reaction activity for material growth for longer time

Grain Size

- Strategy 1 – Decreasing the nucleation density
  - Few nucleation sites – Smooth surface – molten glass at high temperature (Other liquid or quasi-liquid surface)
  - Example – MoS_2 FET – Field effect mobility of $95\,\mathrm{cm^2V^{-1}s^{-1}}$, on/off current ratio of 10^7
  - Using Additives to decrease nucleation density
  - Example – Oxygen introduction – etch away unstable nuclei – large monolayer MoS_2 with domain size $350\,\mu\mathrm{m}$ on sapphire c-plane
- Strategy 2 – Maintaining reaction activity of grain growth for longer time
  - Decreasing the energy barrier for the reaction
  - Self-limited catalytic surface growth mechanisms
  - Examples - large area monolayer WS_2 single crystal of millimeter size on Au foils, MoS_2 of size $80\,\mu\mathrm{m}$ on Au foil, WS_2 of size $135\,\mu\mathrm{m}$ on c-plane sapphire

Grain Size

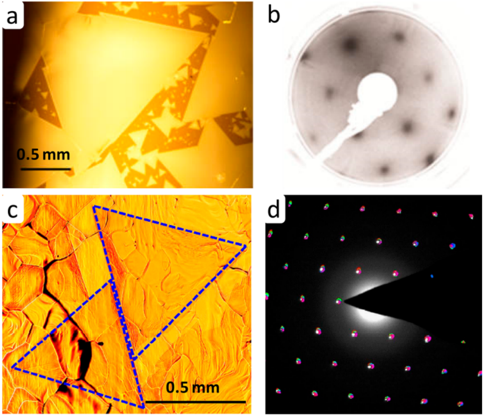


Figure 4. Growing large single crystal 2D materials. (a) Optical image of $MoSe_2$ crystals grown on molten glass. (b) LEED pattern of $MoSe_2$ crystal. (c) Optical image of millimeter-size triangular monolayer single crystal WS_2 domains grown on Au foil. (d) Superimposed image of 12 SAED patterns taken from different parts of the same WS_2 domain, confirming it is a single crystal. (a, b) Reprinted from ref 75. Copyright 2017 American Chemical Society. (c, d) Reprinted with permission from ref 26. Copyright 2015, Rights Managed by Nature Publishing Group.

Remaining Topics to Discuss

- Layers, Orientation, Morphology, Phase, Doping, Quality and Defects
- CVD growth of wafer scale continuous 2D materials films
- CVD growth of 2D material based heterostructure
- Application of CVD-grown 2D materials and their heterostructure
- Conclusion
- Epitaxial growth of 2D Layered TMDCs: Growth Mechanism, Controllability and Scalability

Descriptions

CVD	Chemical Vapour Deposition
TMDCs	Transition Metals Dichalcogenides
PTAS	Perylene-3,4,9,10-tetracarboxylic dianhydride
PTCDA	Perylene-3,4,9,10-tetracarboxylic dianhydride
rGO	reduced Graphene Oxide
PECVD	Plasma Enhanced CVD
ICP-CVD	Inductively Coupled Plasma CVD
FET	Field Effect Transistor

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Thank You!