Advanced CVD Technology for Emerging 2D Materials

*Kevin Chung-Che Huang**, *Nikolaos Aspiotis, Ghadah A. Alzaidy, Qingsong Cui, Ed Weatherby, Chris Craig, Katrina Morgan, Ioannis Zeimpekis and Daniel W. Hewak*

Optoelectronics Research Centre, University of Southampton, Southampton, SO17 1BJ, U.K.
**E-mail: cch@orc.soton.ac.uk*

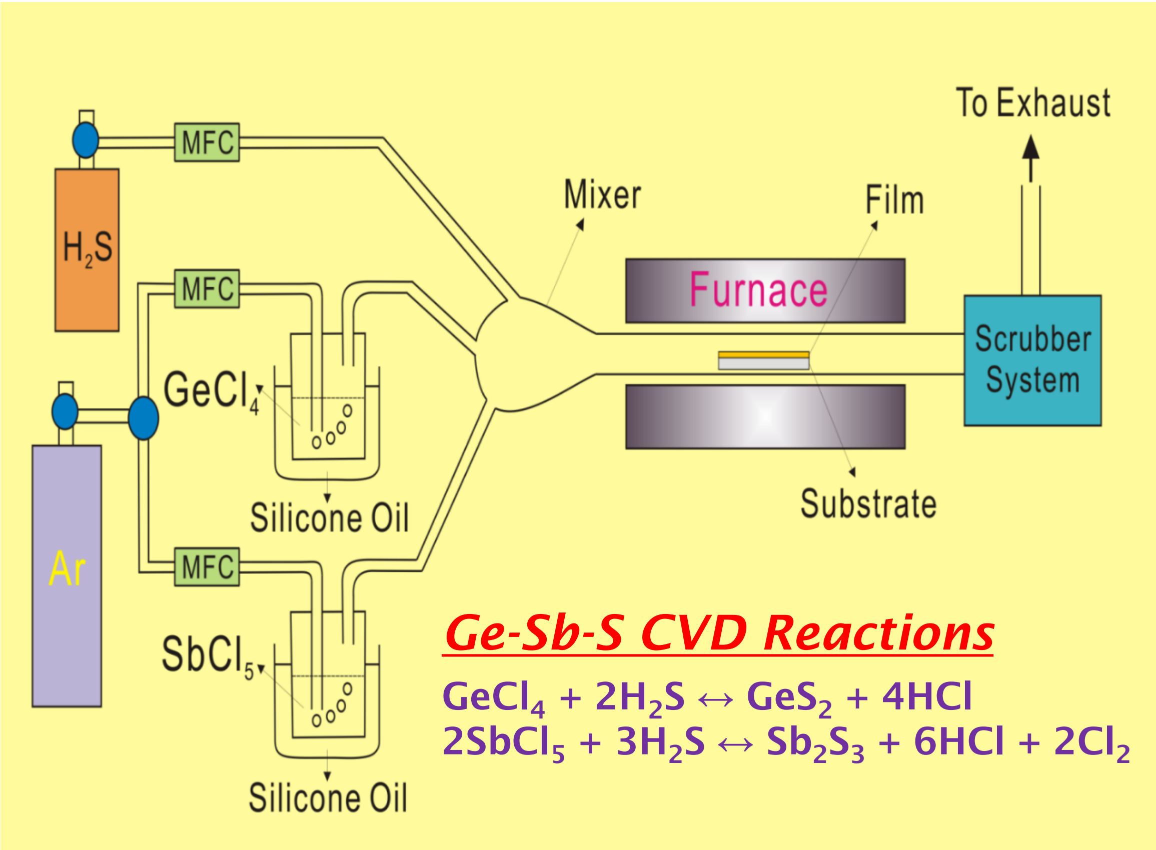
Outline:

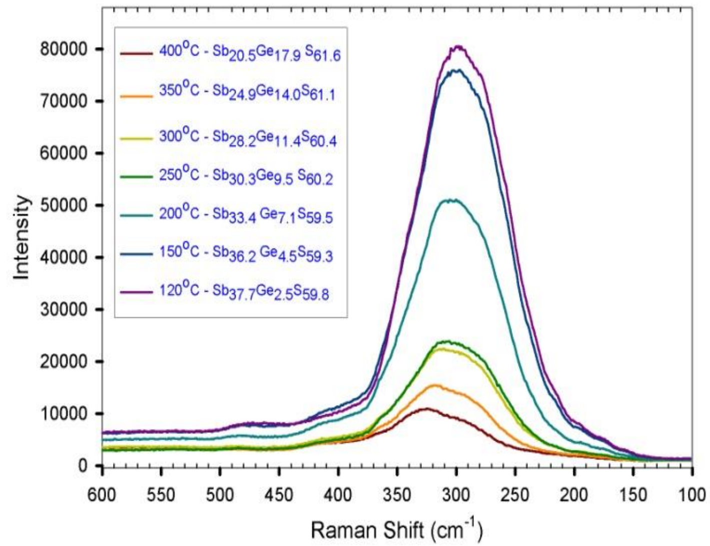
- Overview of CVD activities at the ORC
- CVD for 2D Materials-Graphene
- CVD for 2D Materials-Transition Metal Di-chalcogenides
- Summary

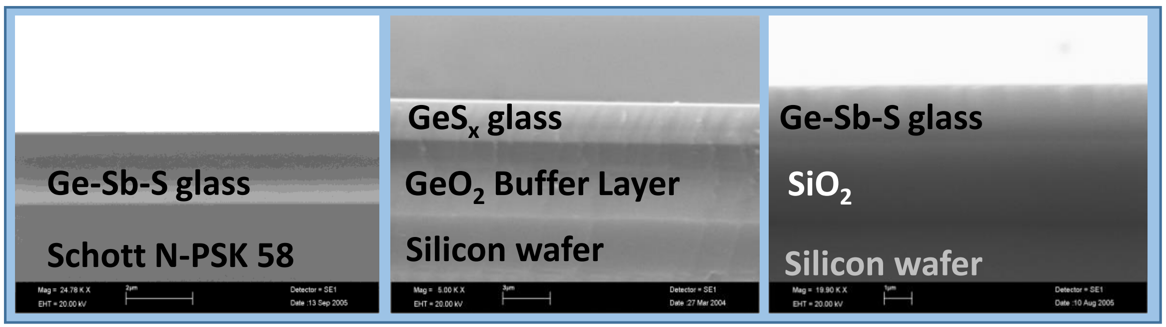
Materials Capability:

Compound Synthesized	Applications
Ge-S, Sb-S, Ge-Sb-S	Optical, Electronics, Nano
Ge-Sb-Te (GST), Ge-Sb	Electronics, PCRAM
Ti-S	Tribology, Battery, Thermoelectric
Sn-S	Transistor, Solar, Semiconductor
Mo-S, Mo-Se	Transistor, Tribology
W-S, W-Se	Transistor, Tribology
Cu-In-Ga-S / Se (CIGS), Cu-Zn-Sn-S (CZTS), Cu-Sb-S	Solar
Ti-O	Transparent conducting oxides, solar, Filtration
Zn-O	Transparent conducting oxides, solar
Sn-O	Transparent conducting oxides, solar
Sb-O/Sb-S, Ge-O/Ge-S, Mo-O/Mo-S	Memristor
Graphene	Solar, Transistor,
BN	Graphene family
Zn-S	Mid-IR
Bi-O-X	Photocatalyst
Bi-S, Bi-Se	Thermoelectric, topological insulator
V-O, V-S, V-Se	Thermochromic, 2D materials
Ta-S, Ta-Se	2D materials
Ga-S, Ga-Se	2D materials
Nb-S, Nb-Se	2D materials

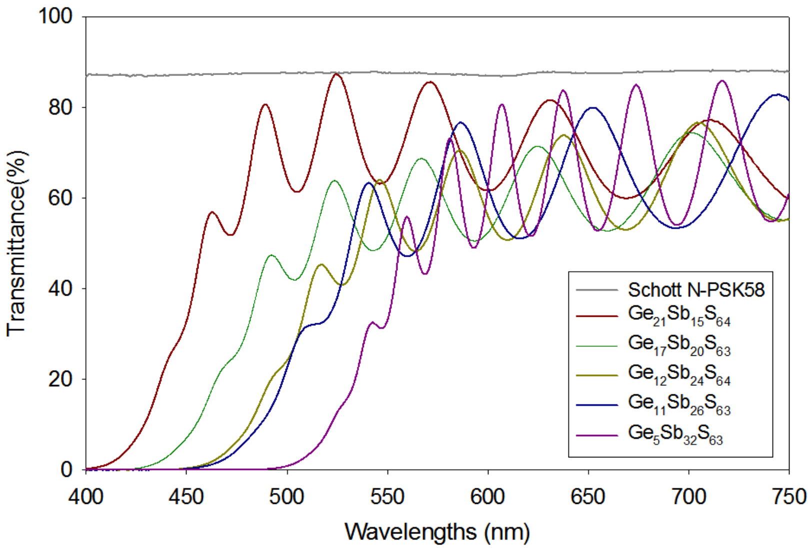
CVD apparatus for Ge-S and Ge-Sb-S fabrication

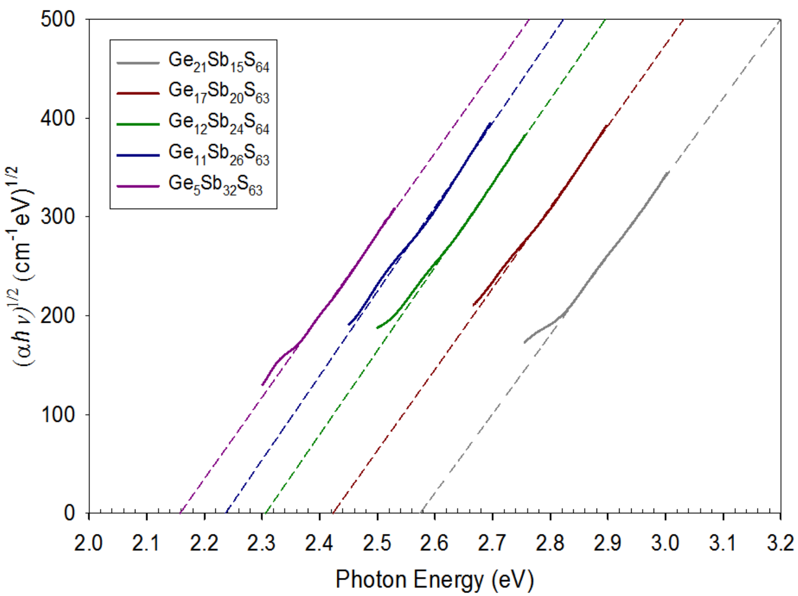


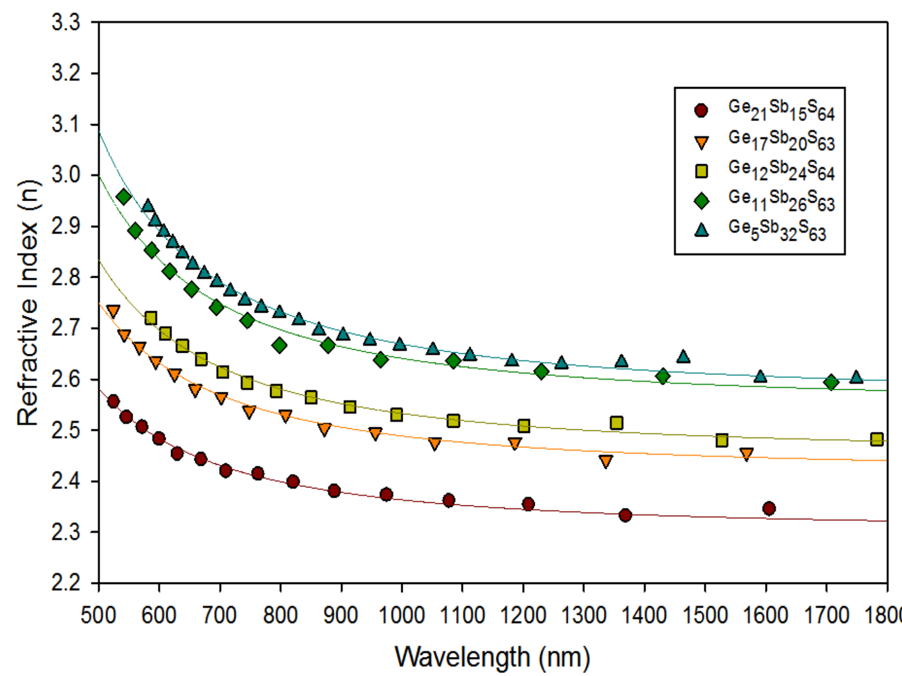


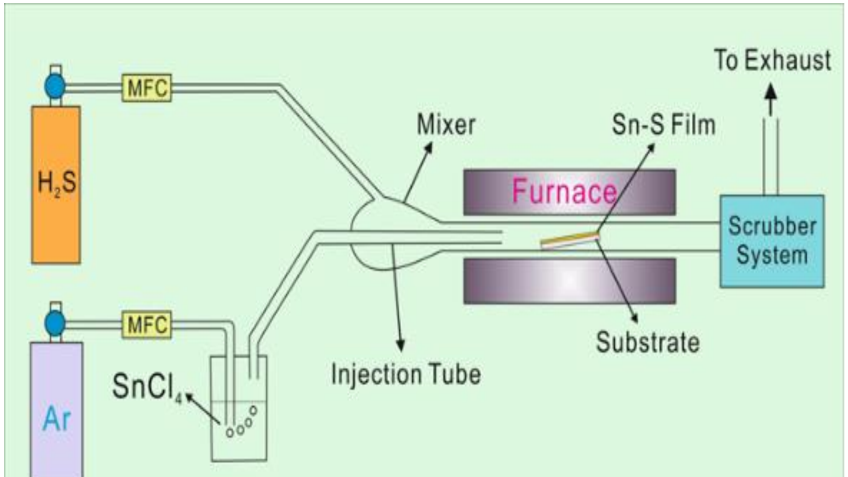


Optical properties of CVD-grown Ge-Sb-S thin films

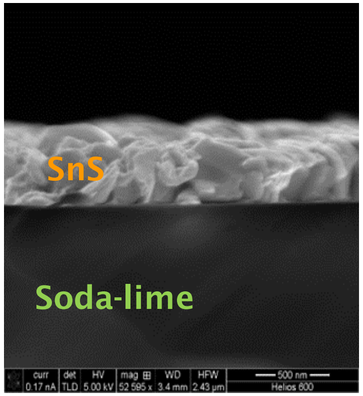




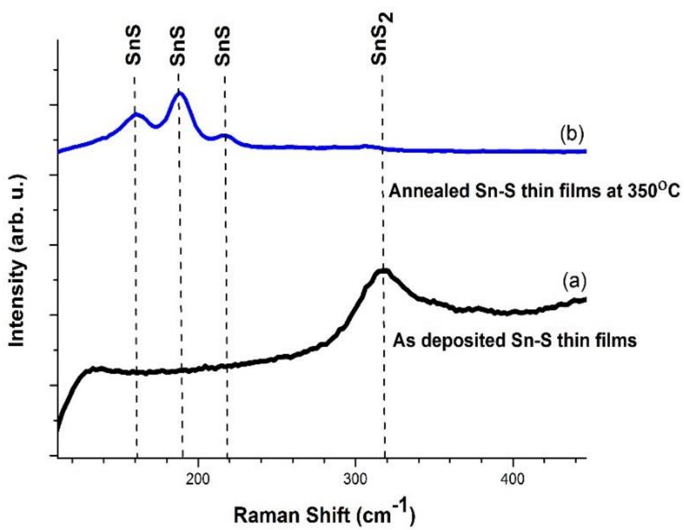


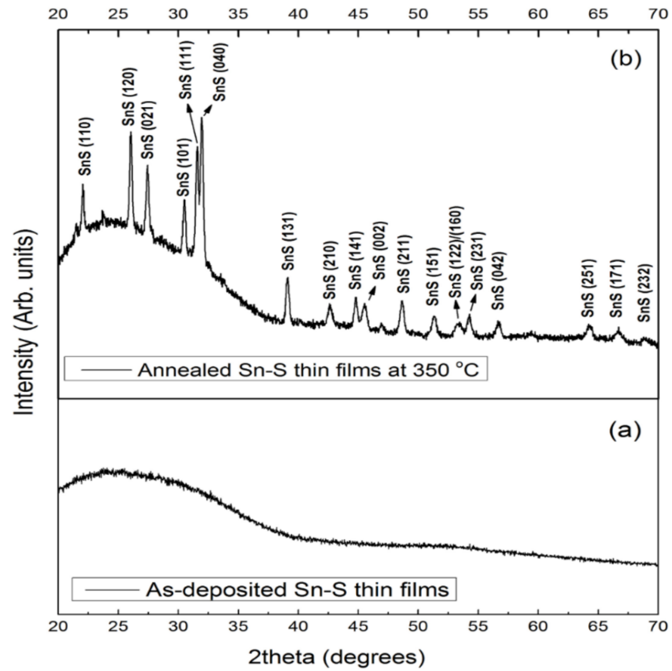


$$SnCl_4 + 2H_2S \rightarrow SnS_2 + 4HCl$$



Tin sulphide Fabricated by CVD

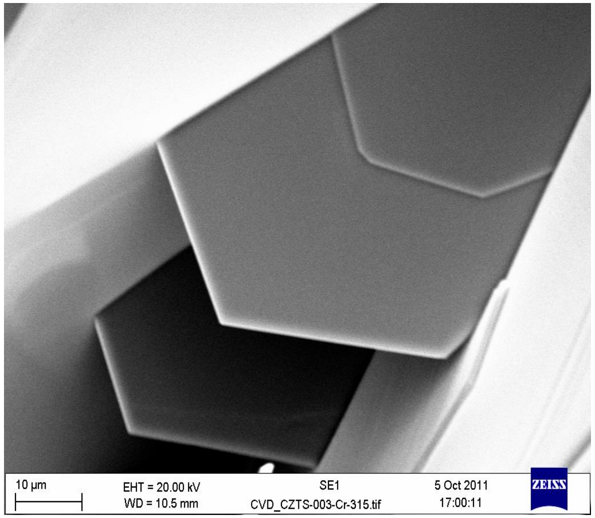


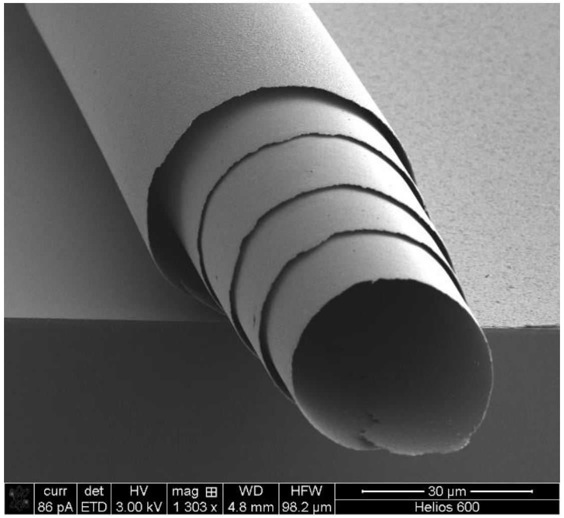


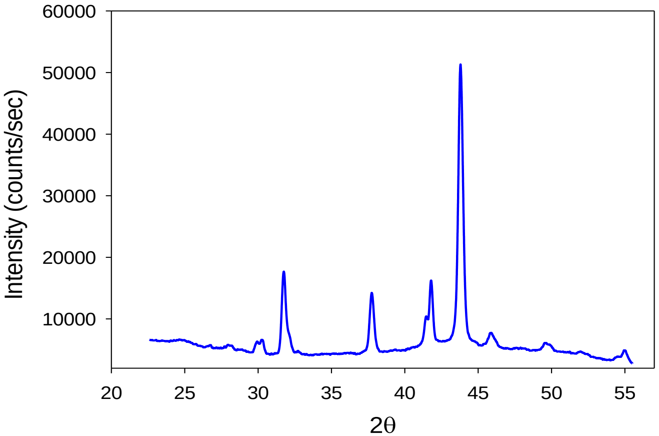
Raman spectra of (a) room temperature as-deposited Sn-S thin film and (b) annealed Sn-S thin film at 350 °C.

XRD patterns of (a) room temperature as-deposited Sn-S thin film and (b) annealed Sn-S thin film at 350 °C

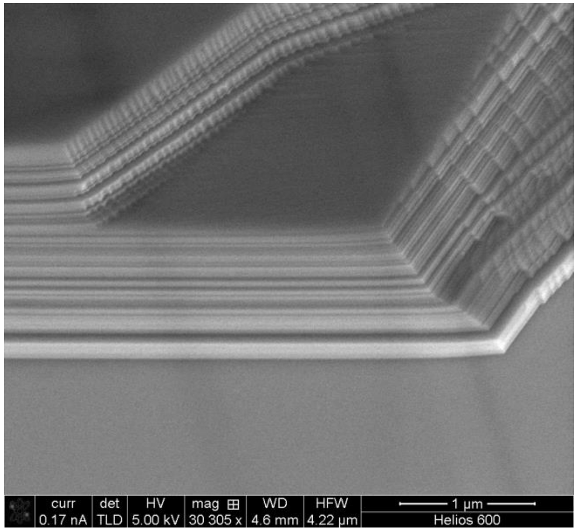
SnS_2 crystals grown by APCVD

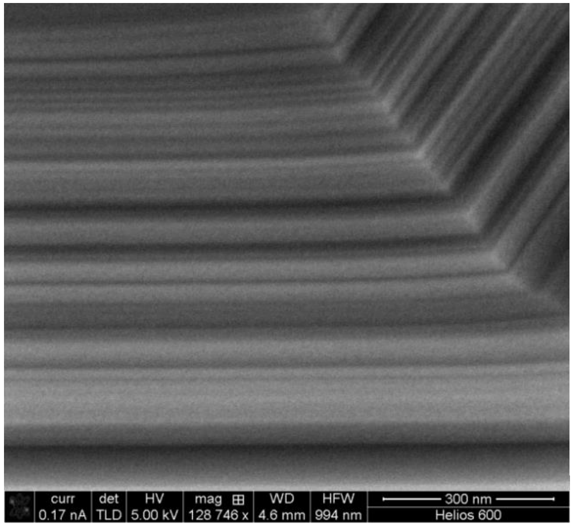


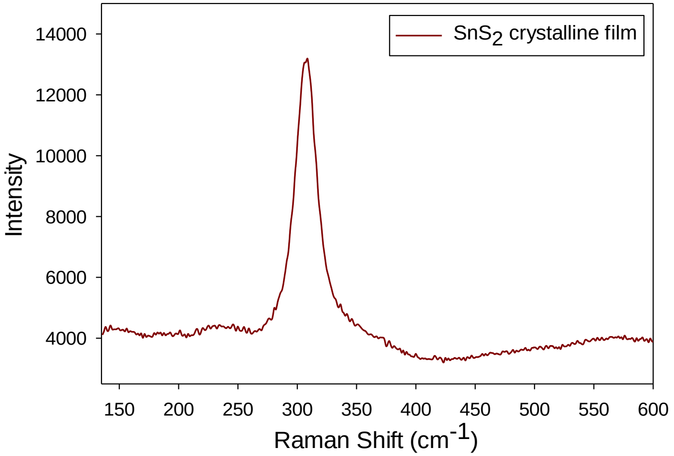




XRD patterns of SnS_2 thin film







Raman spectra of SnS_2 thin film

Background:

Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenIdes	MoS_2, WS_2, $MoSe_2$, WSe_2	Semiconducting dichalcogenides: $MoTe_2$, WTe_2, ZrS_2, $ZrSe_2$ and so on	Metallic dichalcogenides: $NbSe_2$, NbS_2, TaS_2, TiS_2, $NiSe_2$ and so on	Layered semiconductors: GaSe, GaTe, InSe, Bi_2Se_3 and so on	
2D oxides	Micas, BSCCO	MoO_3, WO_3	Perovskite-type: $LaNb_2O_7$, $(Ca,Sr)_2Nb_3O_{10}$, $Bi_4Ti_3O_{12}$, $Ca_2Ta_2TiO_{10}$ and so on	Hydroxides: $Ni(OH)_2$, $Eu(OH)_2$ and so on	
	Layered Cu oxides	TiO_2, MnO_2, V_2O_5, TaO_3, RuO_2 and so on		Others	

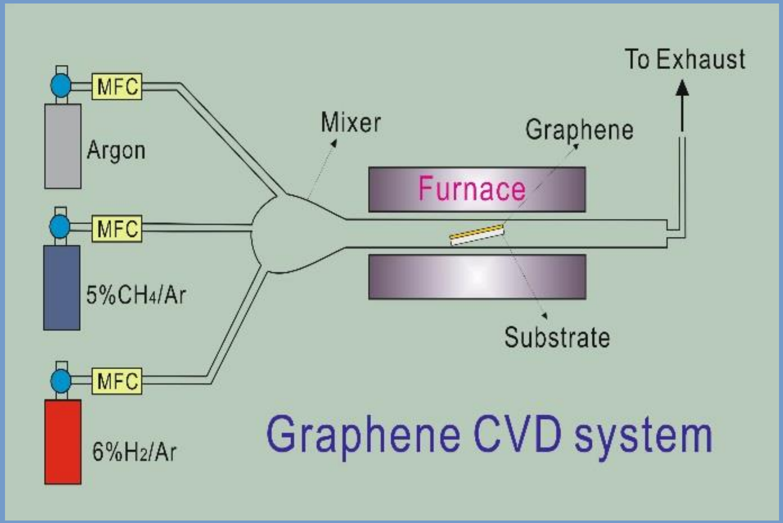
25 JULY 2013 | VOL 499 | NATURE | 419

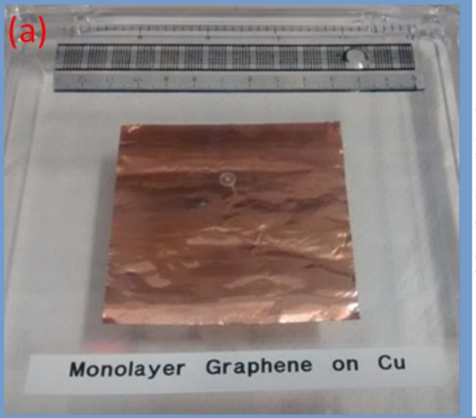
2D materials:

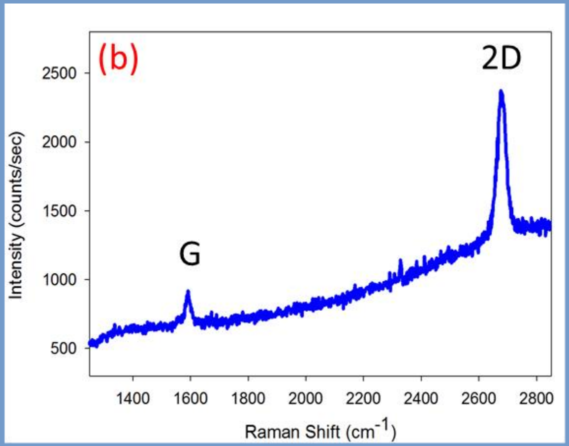
- *Graphene*
- *BN*
- *$(Bi,Sb)_2(Se,Te)_3$*
- *Transition Metal Di-chalcogenides (TMDCs) with sizable bandgaps of 1-2 eV.*

MX_2 , M= Ti, Zr, Hf (group 4)
M= V, Nb, Ta (group 5)
M= Mo, W (group 6)
M= Sn (group 14)
X= S, Se, Te (chalcogen)

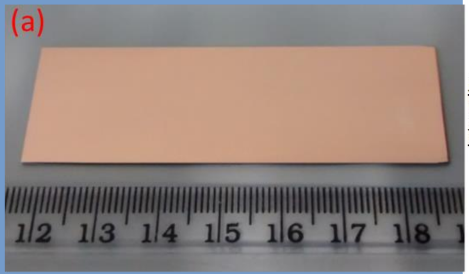
Graphene fabrication

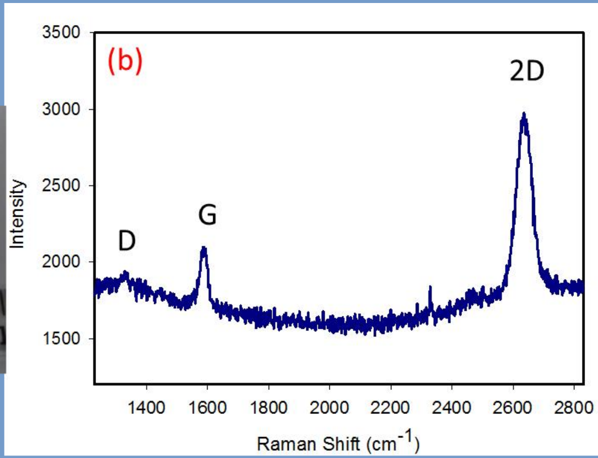






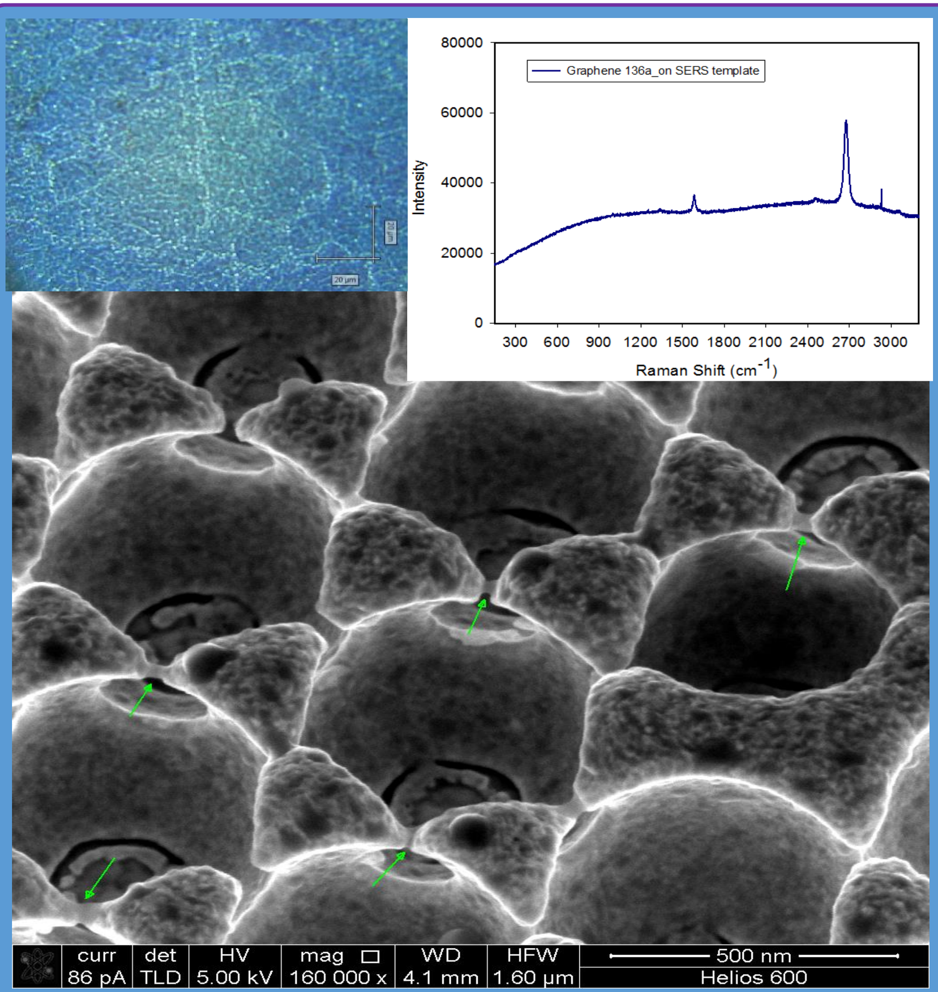
CVD-grown monolayer Graphene on Cu foil



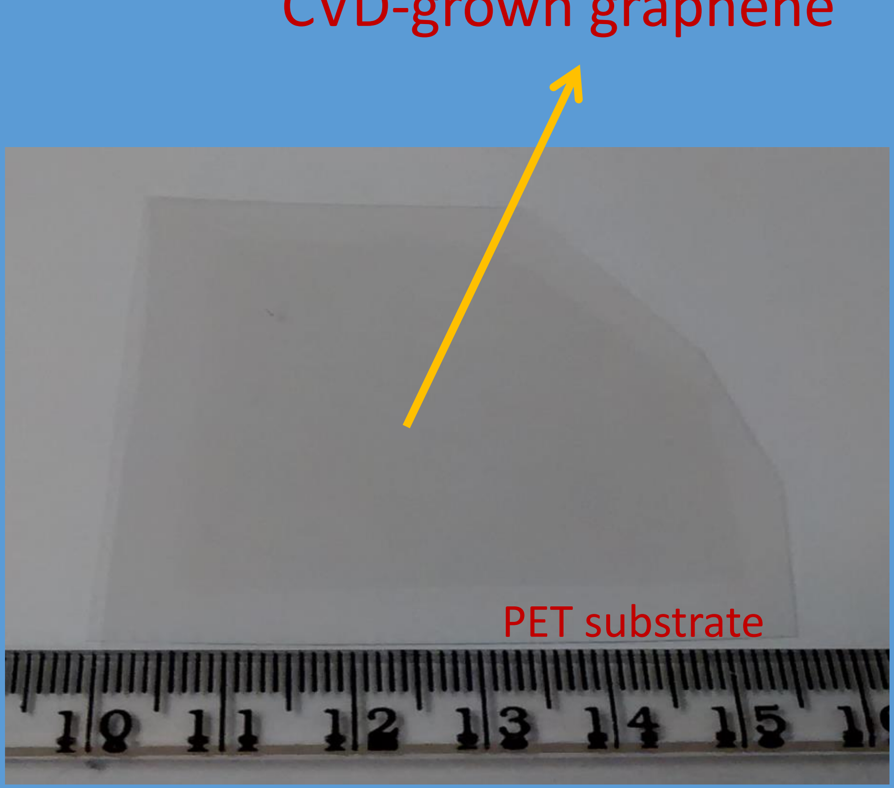


CVD-grown monolayer Graphene on Cu/SiO_2/Si substrate

➢ CVD-grown Graphene transfer



CVD-grown Graphene transferred on SERS template substrate



CVD-grown Graphene transferred on flexible PET substrate

Background:

Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
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25 JULY 2013 | VOL 499 | NATURE | 419

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- *Transition Metal Di-chalcogenides (TMDCs) with sizable bandgaps of 1-2 eV.*

MX_2 , M= Ti, Zr, Hf (group 4)
M= V, Nb, Ta (group 5)
M= Mo, W (group 6)
M= Sn (group 14)
X= S, Se, Te (chalcogen)

Applications of TMDCs:

- Tribology
- Field-effect Transistors
- Flexible and transparent optoelectronics
- Photovoltaics and Photodetectors
- Memory devices
- Gas Sensor (e.g. MoS_2 for NO, NO_2 gas)
- Bio-sensor
- And more to come!

Properties of MoS_2:

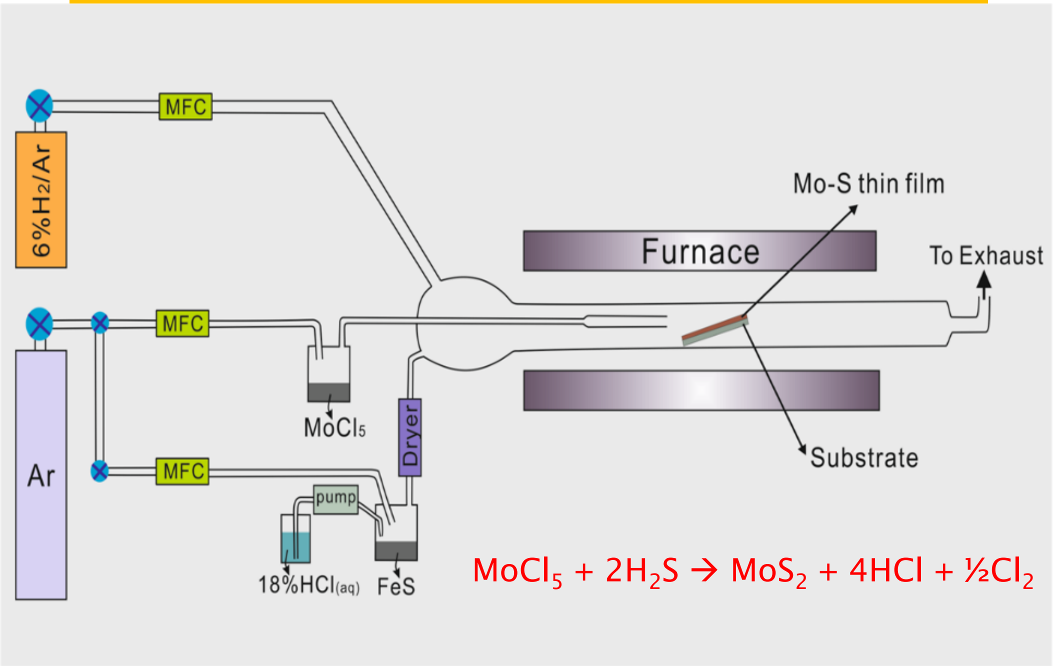
- Sizeable bandgap: 1.2eV (bulk) → 1.8eV (single layer)
- Phonon limit mobility ($cm^2 \cdot V^{-1} \cdot s^{-1}$) at RT: ~410 (similar value to other TMDCs)
- To date, RT mobility of single layer with HfO_2 dielectric ~200 $cm^2 \cdot V^{-1} \cdot s^{-1}$(reduced to ~50 now), 10nm thick MoS_2 thin film transistor device with Sc contact electrodes ~700 $cm^2 \cdot V^{-1} \cdot s^{-1}$
- Mobility of MoS_2 thin films with other reported methods: 0.1-10 $cm^2 \cdot V^{-1} \cdot s^{-1}$

Fabrication of MoS_2:

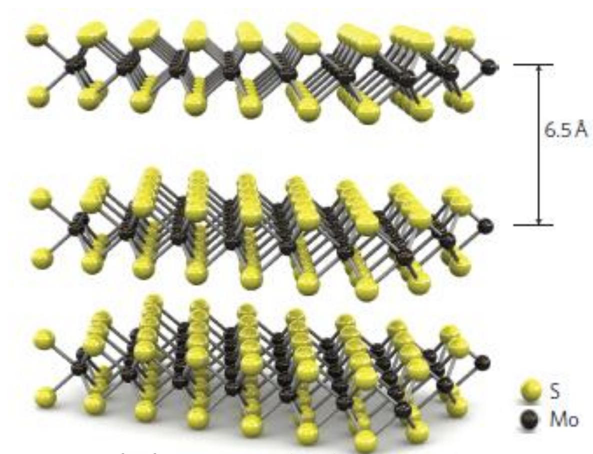
- Exfoliation by micromechanical method
- Exfoliation in solution
- Physical vapour
- Hy
-
- S ybdenum oxides
- Th olysis of the precursors containing Mo and S
- Vapour phase synthesis/Chemical vapour deposition

Current challenge --> A scalable and controllable sample preparation to make large amounts of atomically thin and uniform TMDC layers!

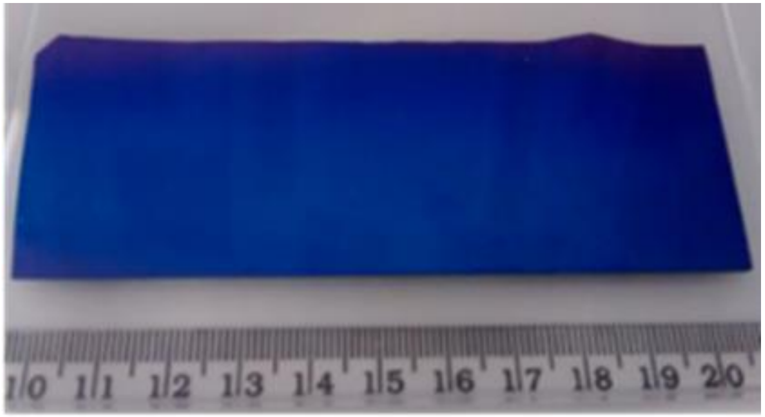
CVD apparatus for MoS_2 thin films



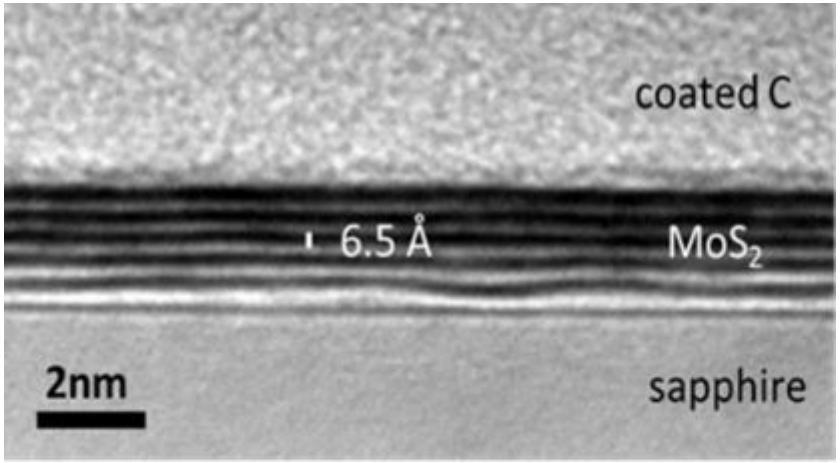
$MoCl_5 + 2H_2S \rightarrow MoS_2 + 4HCl + ½Cl_2$



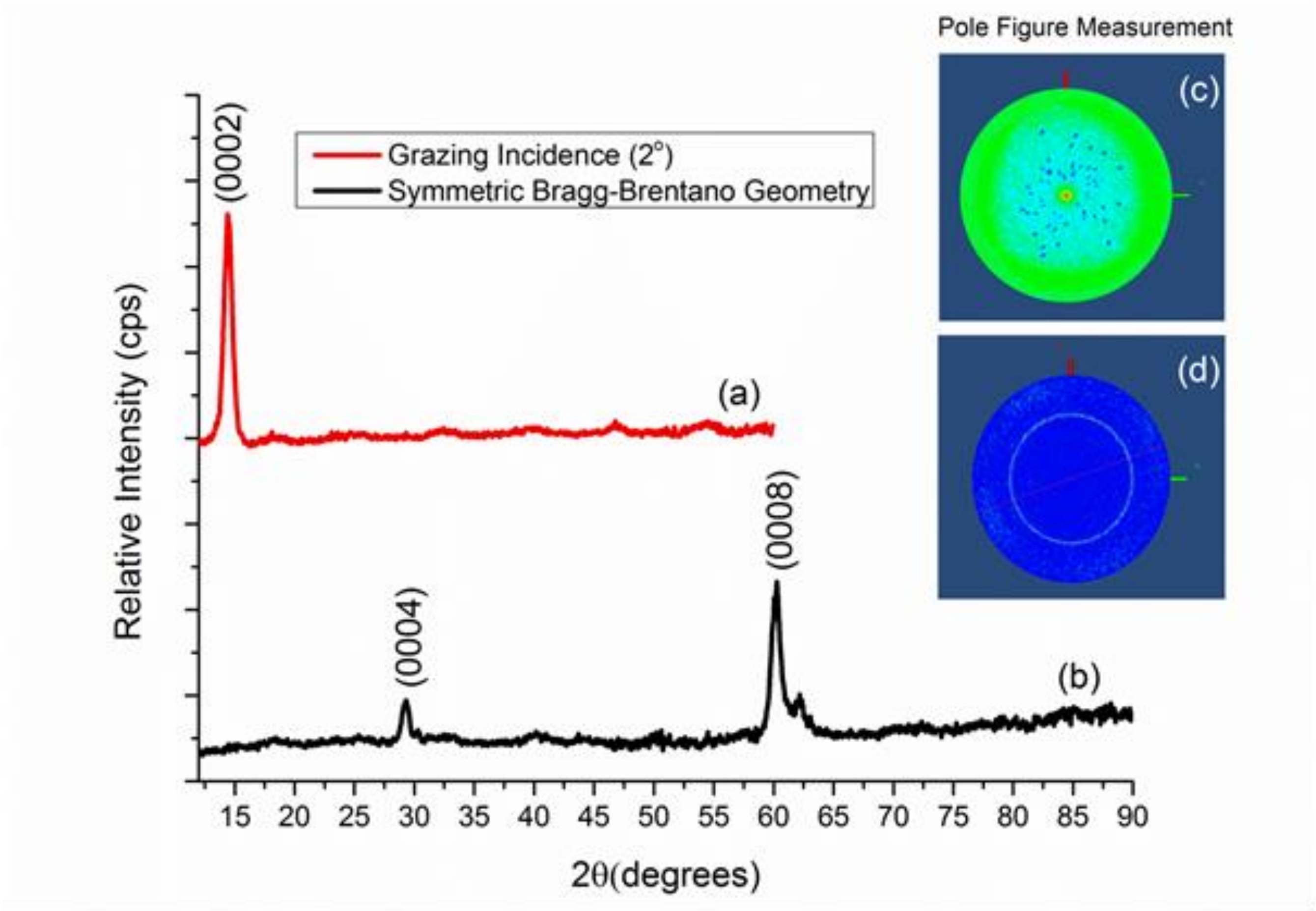
Nature Nanotechnology 6, 147-150 (2011)



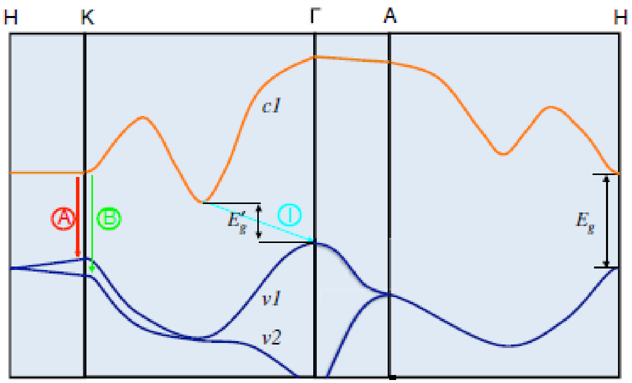
CVD-grown MoS_2 on 295nmSiO_2/Si



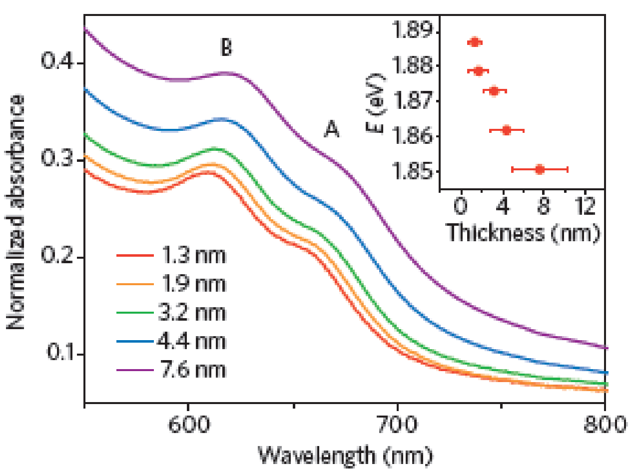
TEM image of CVD-grown MoS_2 on sapphire



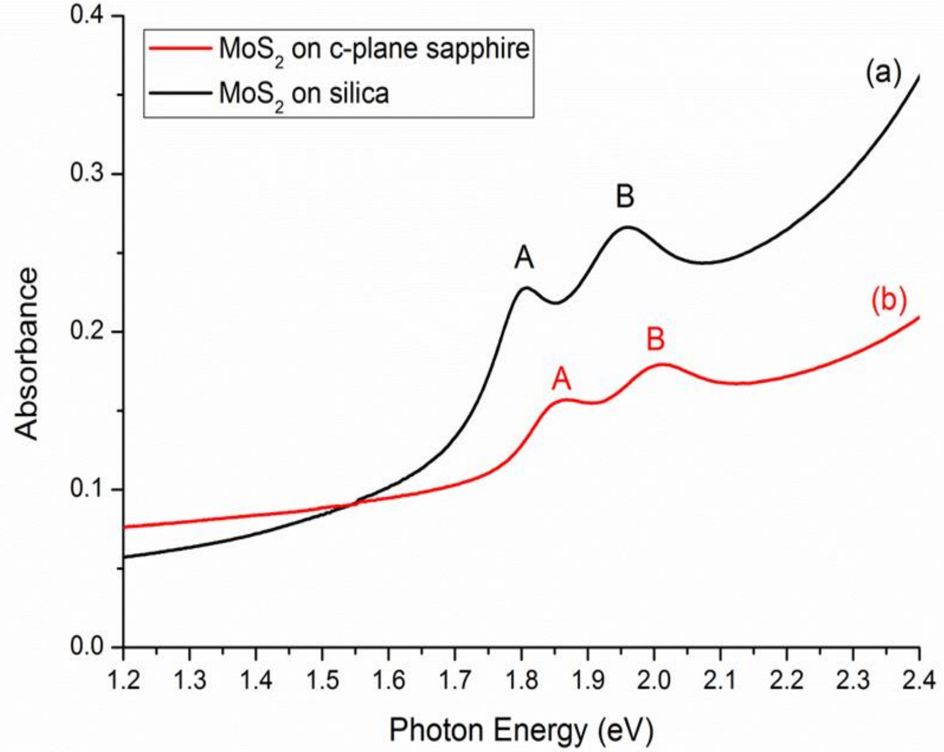
X-ray diffraction patterns of APCVD grown MoS_2 thin film on c-plane sapphire substrate with (a) grazing incidence (2º) setup, (b) symmetric Bragg-Brentano geometry setup (c) pole figure measurement of the 002 plane (d) pole figure measurement of the 103 plane.



PRL **105**, 136805 (2010)



Nano Lett., 2011, 11, 5111–5116



UV-VIS-NIR absorbance spectra of APCVD grown MoS_2 thin films on (a) silica substrate (b) c-plane sapphire substrate.

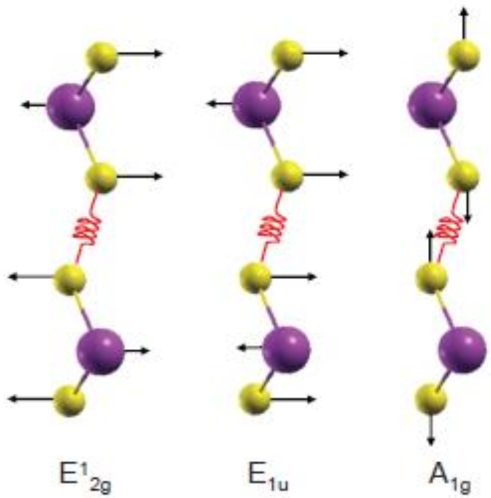
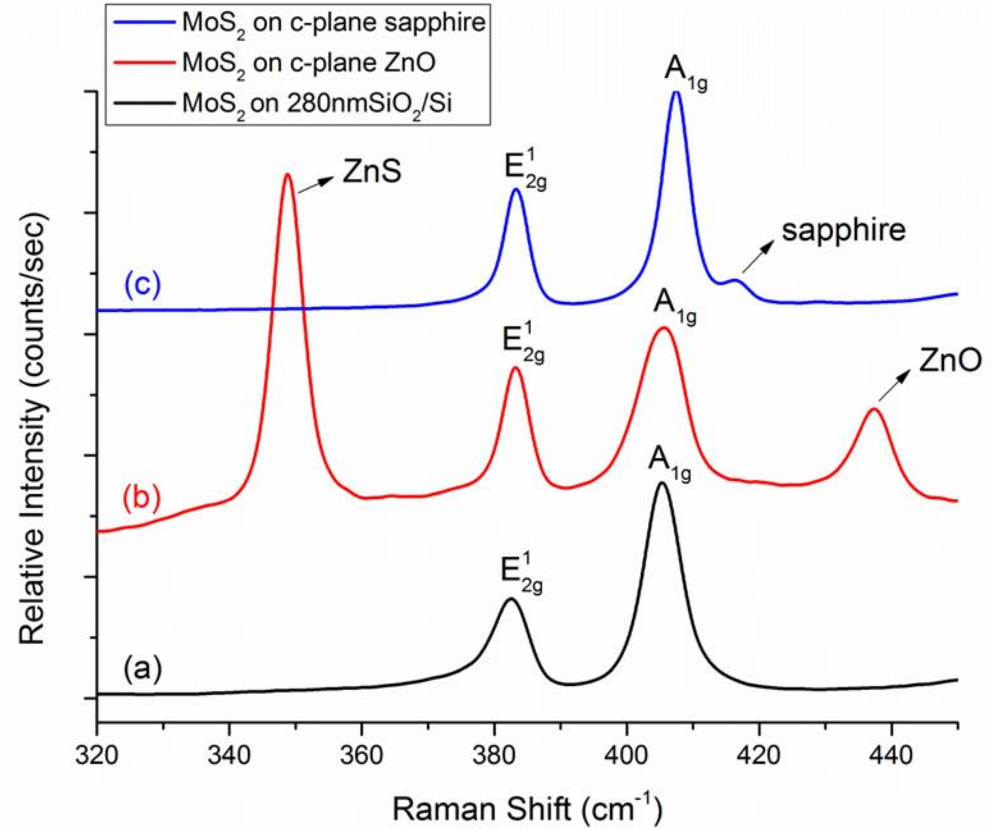
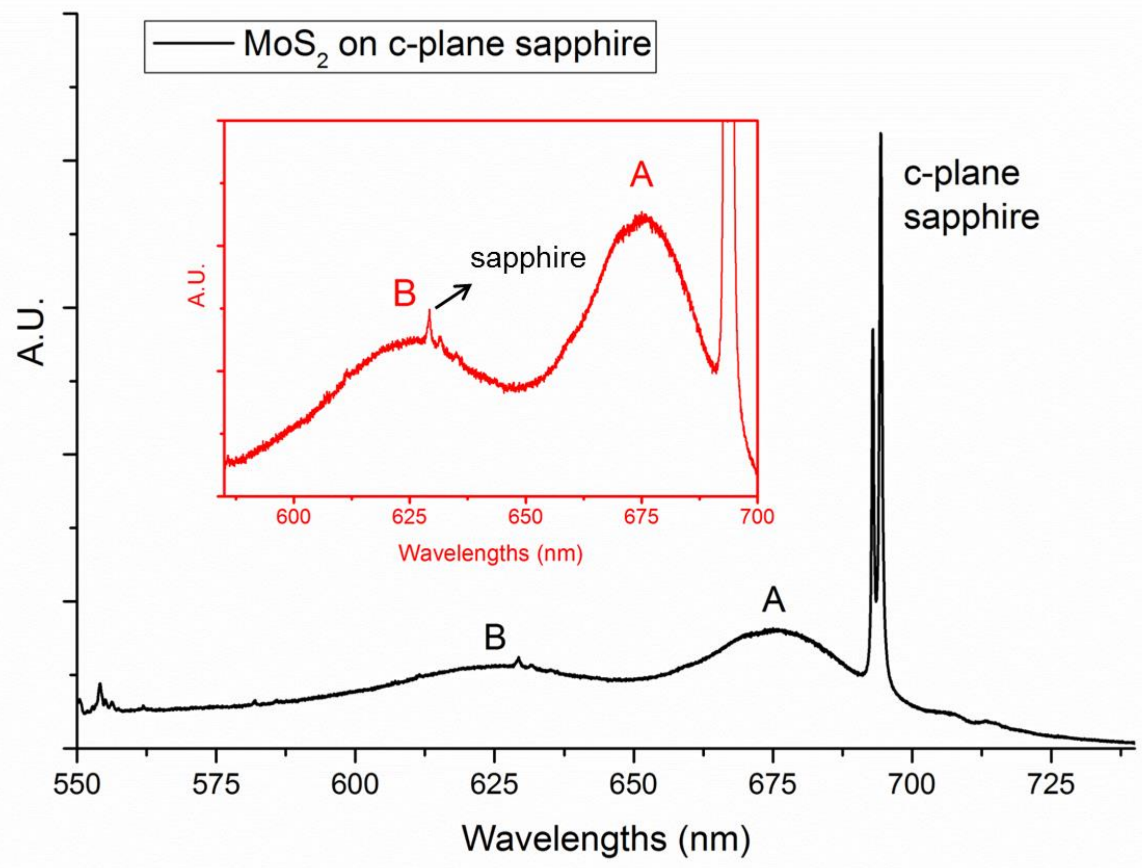


FIG. 3. Phonon modes in-plane E^1_{2g}, E_{1u}, and the out-of-plane phonon mode A_{1g}, for the bulk MoS_2 (analogously for WS_2).

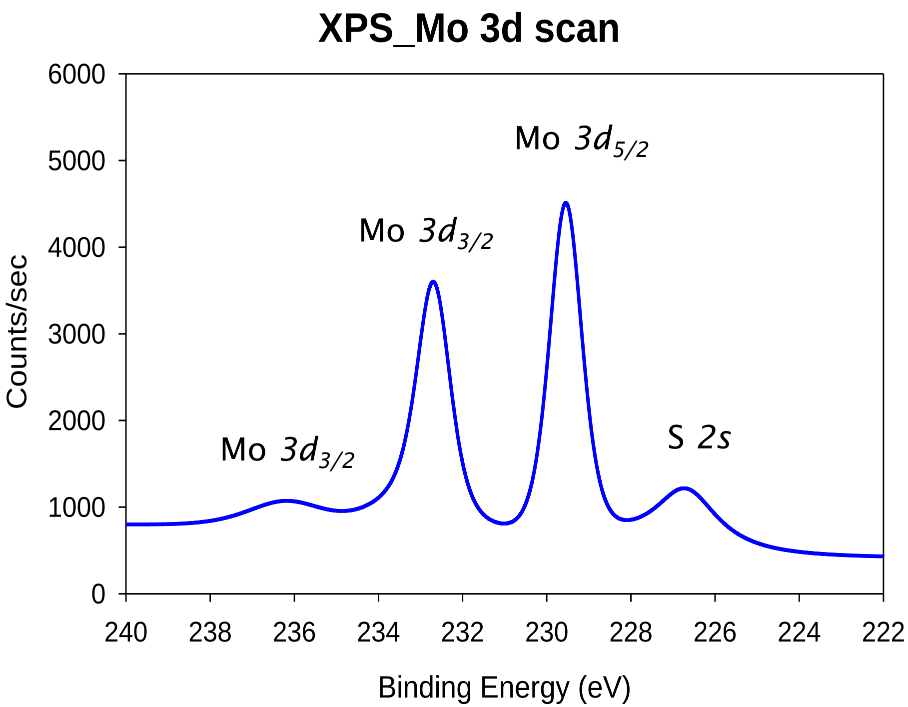
PHYSICAL REVIEW B **84**, 155413 (2011)

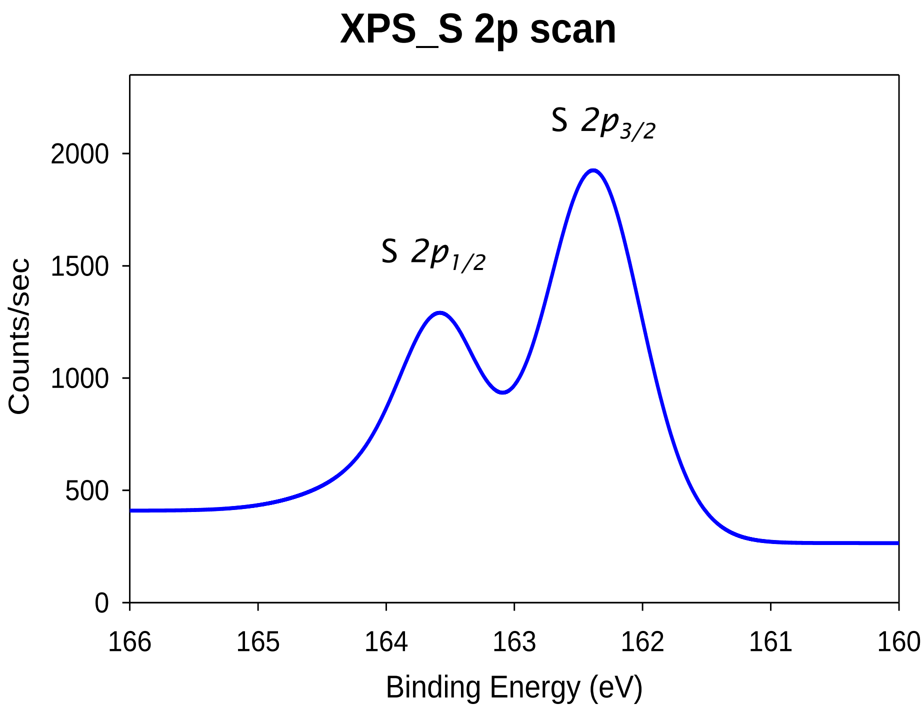


Raman spectra of APCVD grown MoS_2 thin films on (a) 280nm SiO_2/Si substrate (b) c-plane ZnO substrate (c) c-plane sapphire substrate.

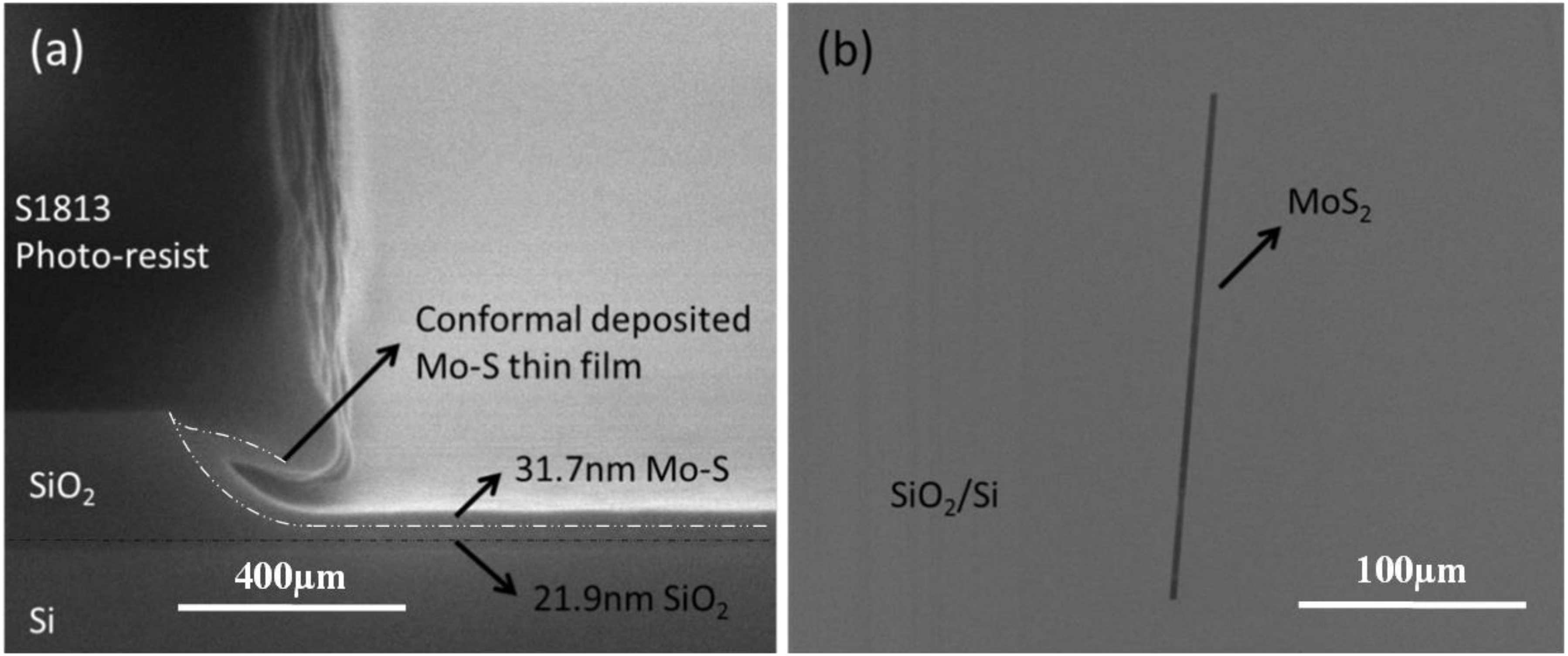


Photoluminescence spectrum of APCVD grown MoS_2 thin film on c-plane sapphire substrate (zoom in peak A and peak B in the inset figure).



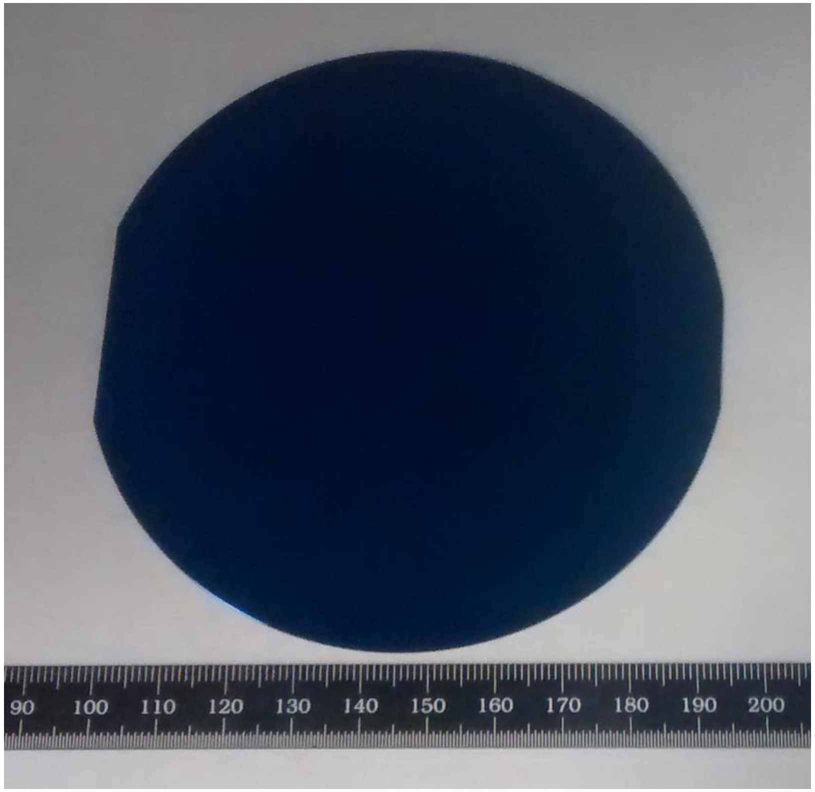


XPS Analysis of APCVD grown MoS_2 on SiO_2/Si

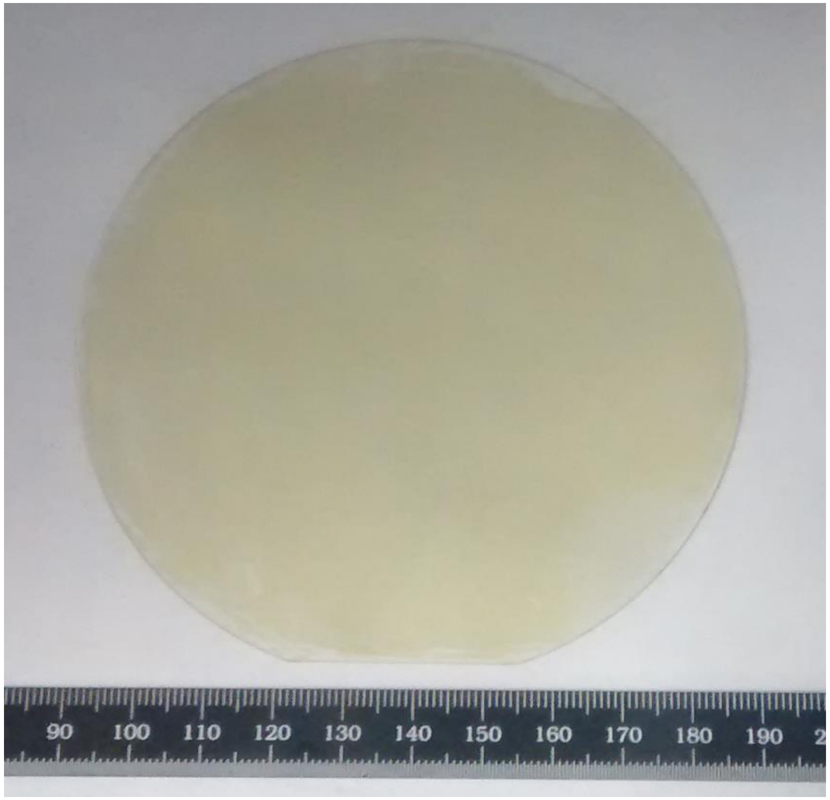


Conformal deposition of MoS_2 thin film on under-cut trenches on 1.1µm spin-coated S1813 photoresist on 200 nm SiO_2/Si substrate

Wafer-scale CVD process for MoS_2



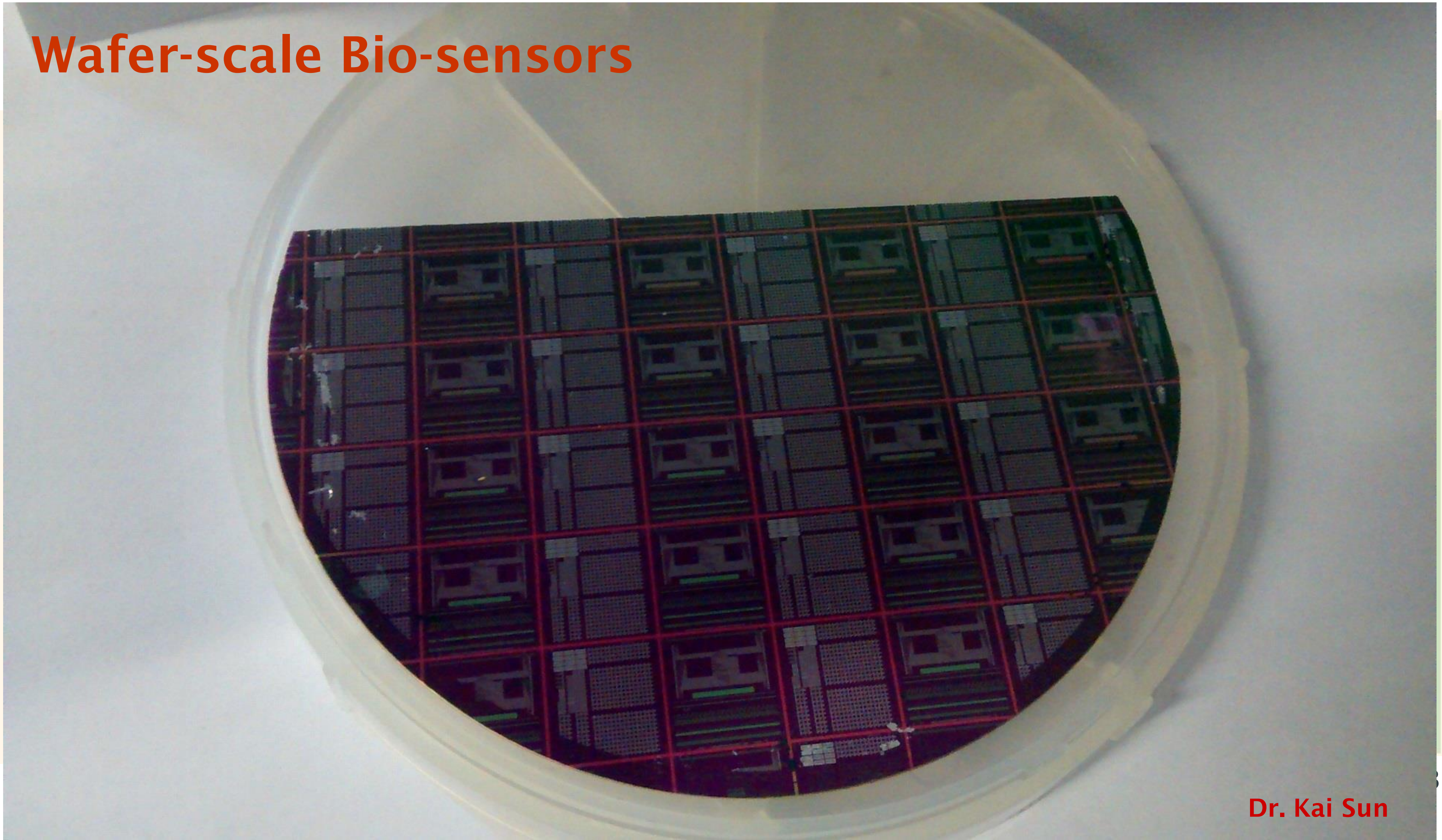
CVD-grown MoS_2 on 4” 300nm/Si wafer



CVD-grown MoS_2 on 4” quartz wafer

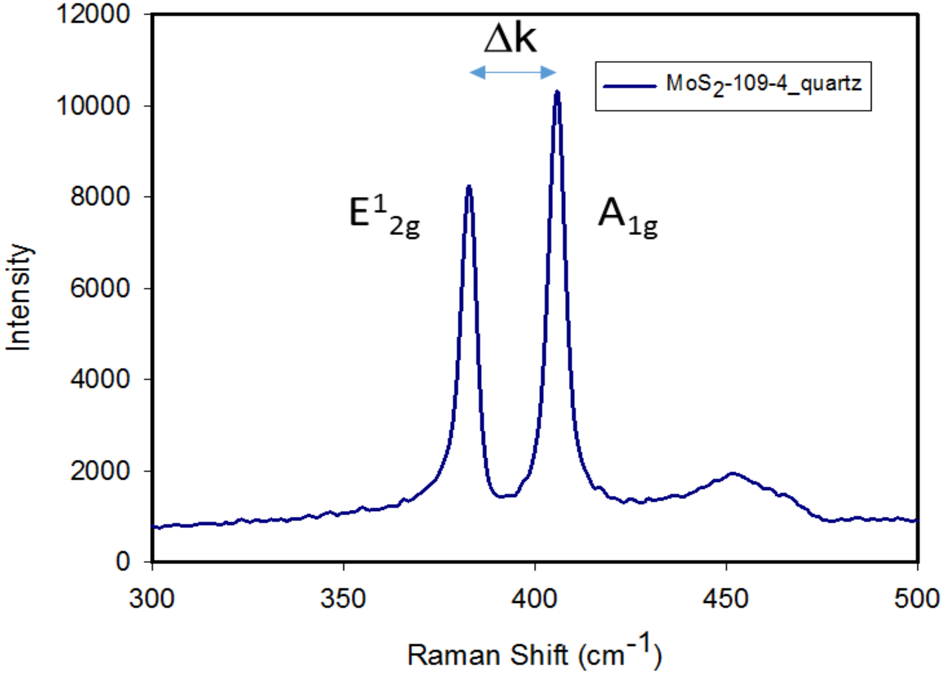
MoS_2 Field-Effect Transistor for Next-Generation Label-Free Biosensors

Wafer-scale Bio-sensors

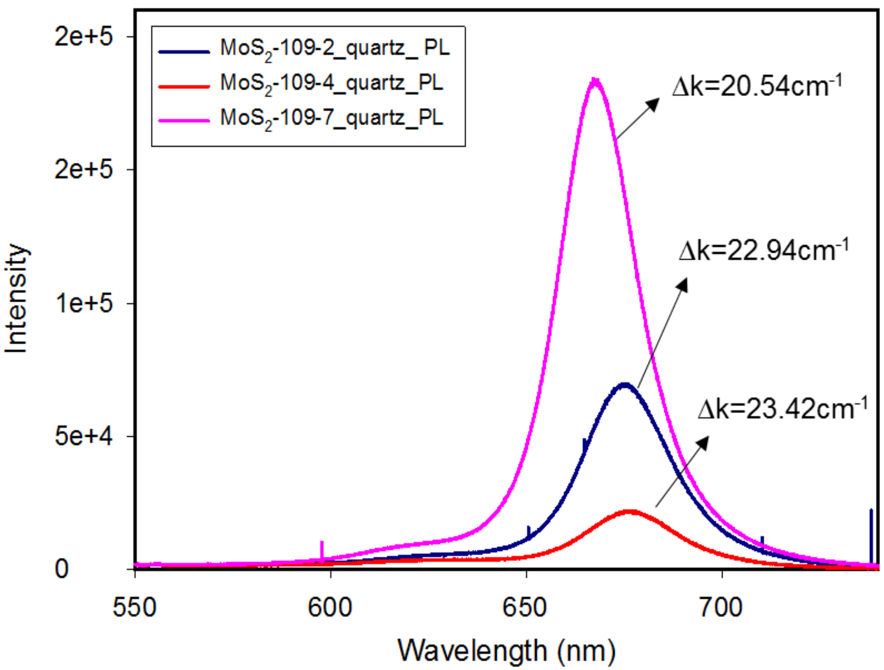


Dr. Kai Sun

Characterizations of CVD-grown MoS_2

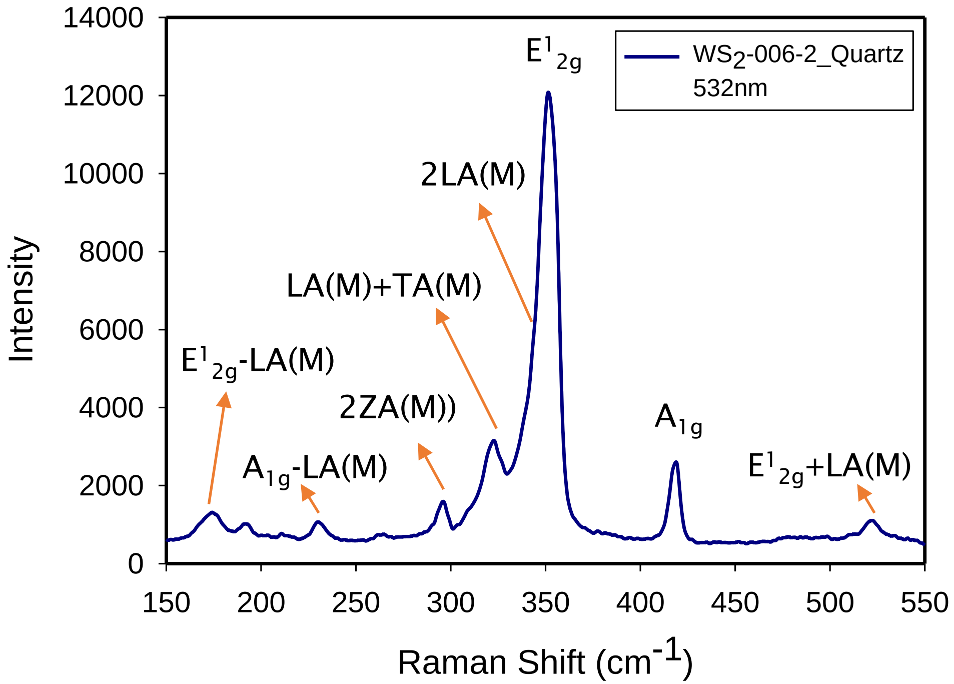


Raman spectra of CVD-grown MoS_2 on quartz

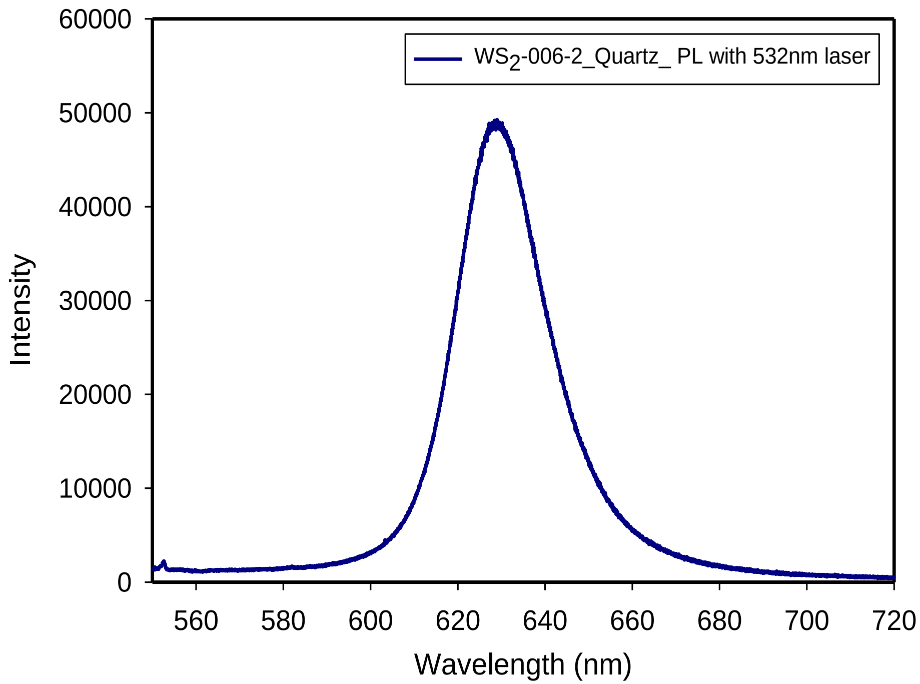


Photoluminescence of CVD-grown MoS_2 on quartz

Characterizations of CVD-grown WS_2

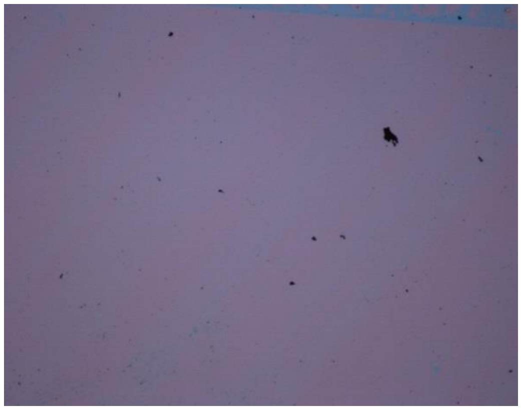


Raman spectra of CVD-grown WS_2 on quartz



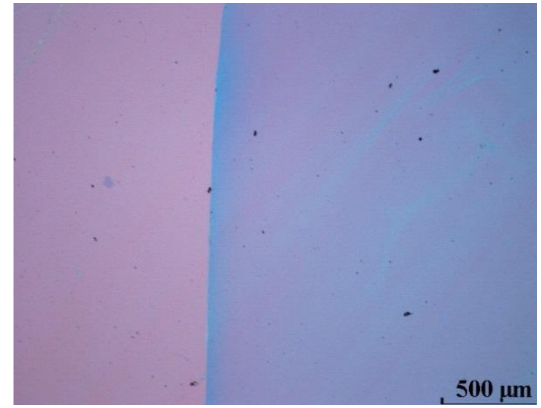
Photoluminescence of CVD-grown WS_2 on quartz

Homogeneous transfer of TMDC's

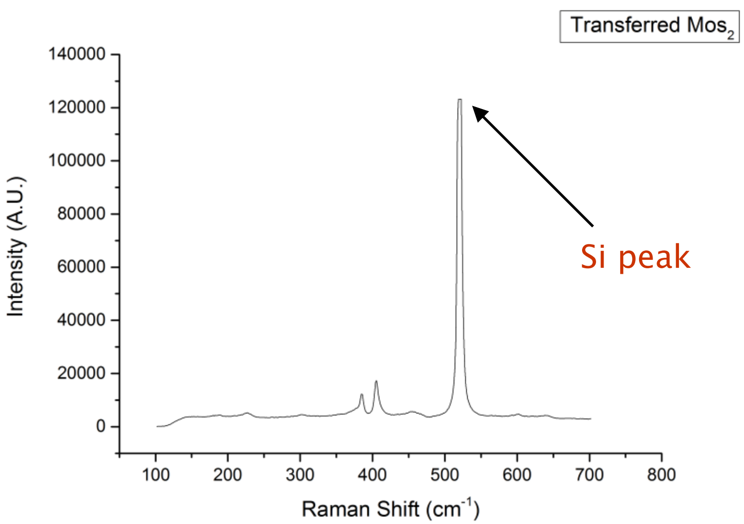


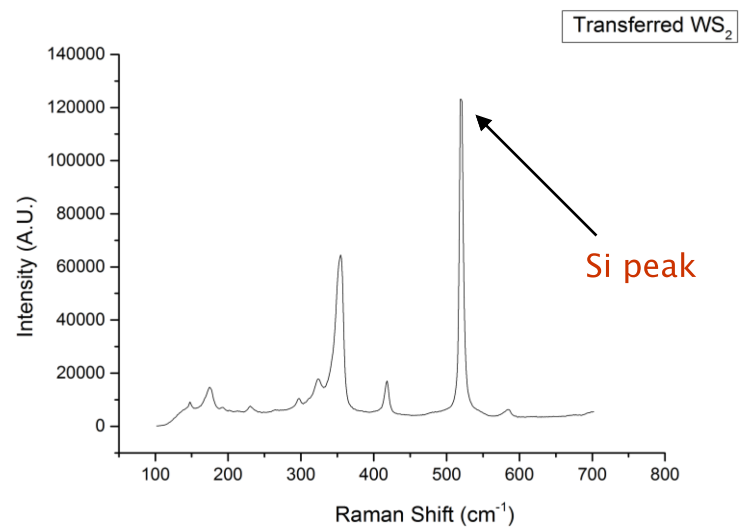
Bare Si/SiO_2 substrate

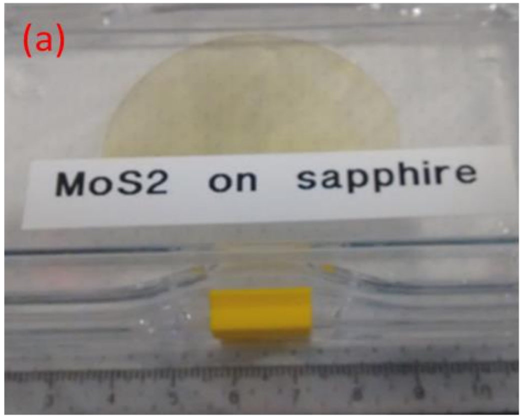
MoS_2 transferred on Si/SiO_2 substrate

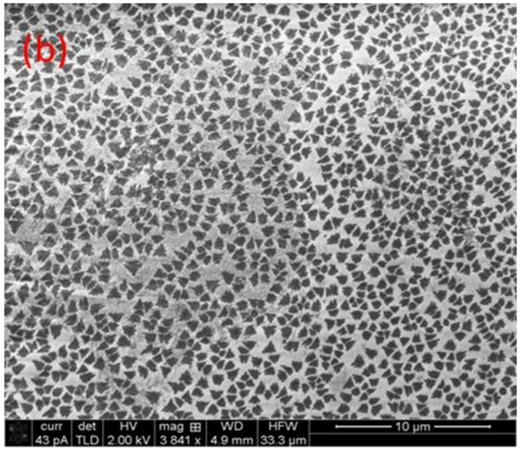


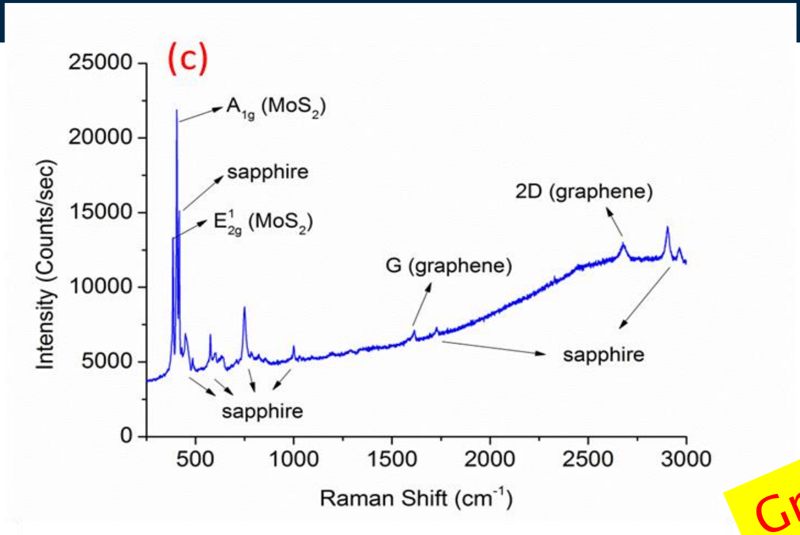
MoS_2 - Si/SiO_2 optical contrast

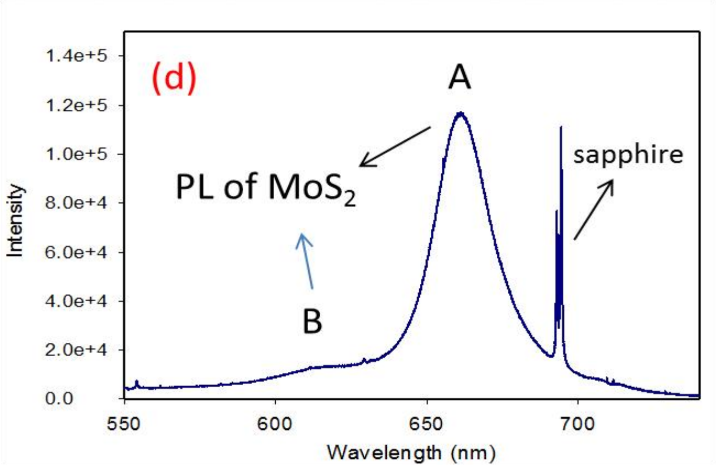








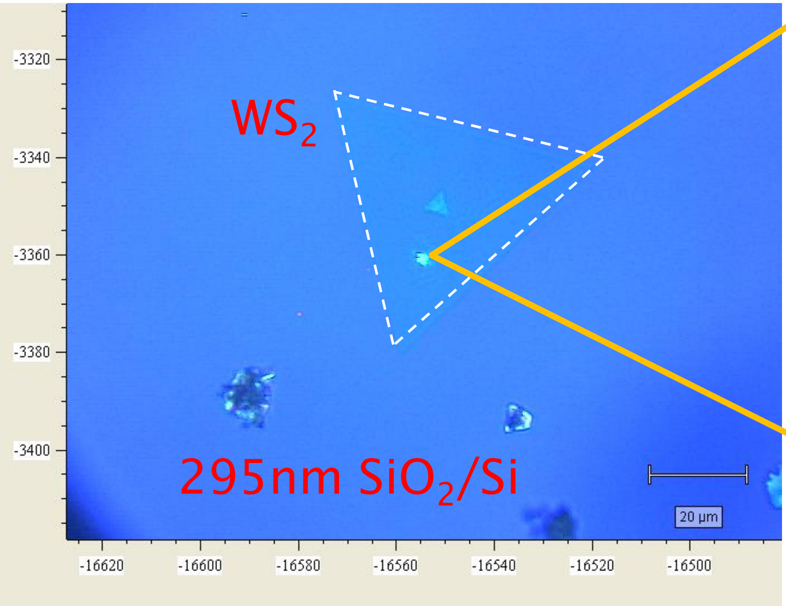




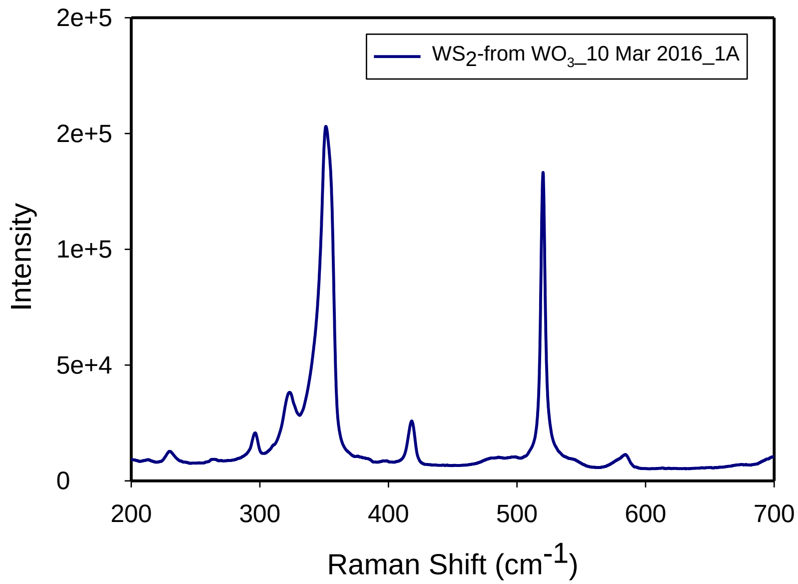
Graphene/MoS_2 heterostructures

(a) CVD epitaxially grown MoS_2 thin thin on c-plane sapphire (0001) substrate (b) SEM image of CVD grown graphene/MoS_2 flakes heterostructures (c) Raman spectrum of CVD grown graphene/MoS_2 flakes heterostructures thin film on c-plane sapphire (0001) substrate (d) photo-luminescence (PL) spectrum of CVD grown graphene/MoS_2 flakes heterostructures thin film on c-plane sapphire (0001) substrate.

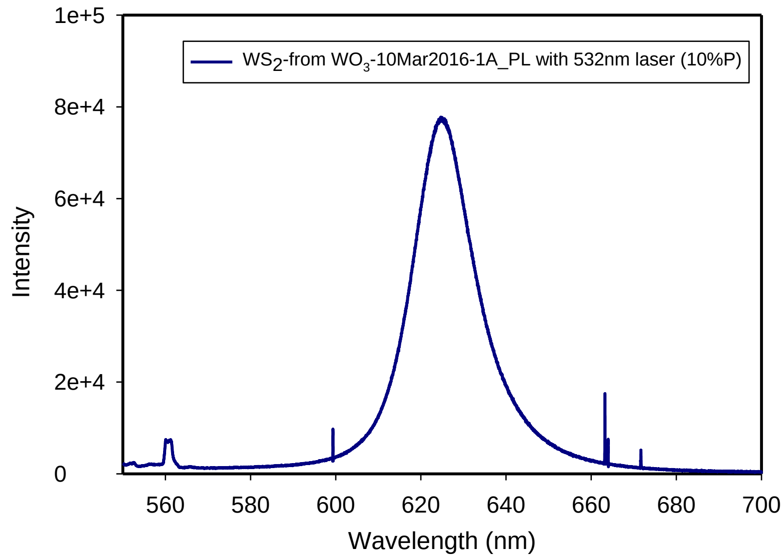
Monolayer single crystal WS_2



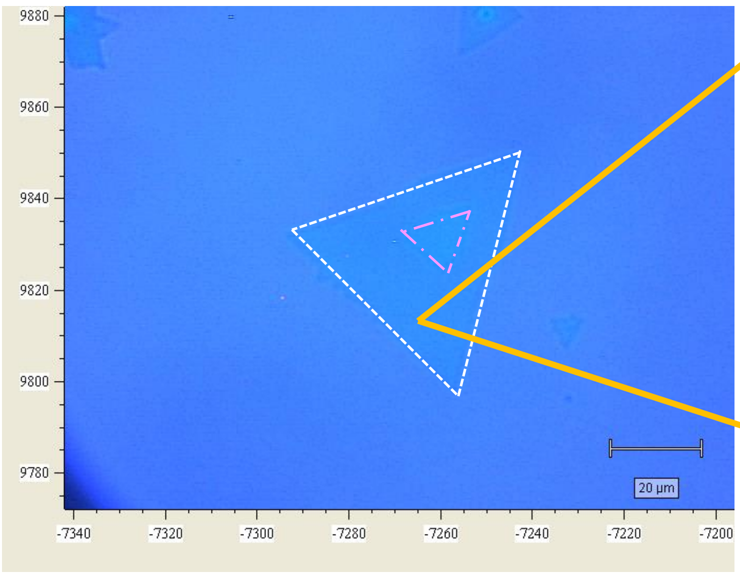
Raman



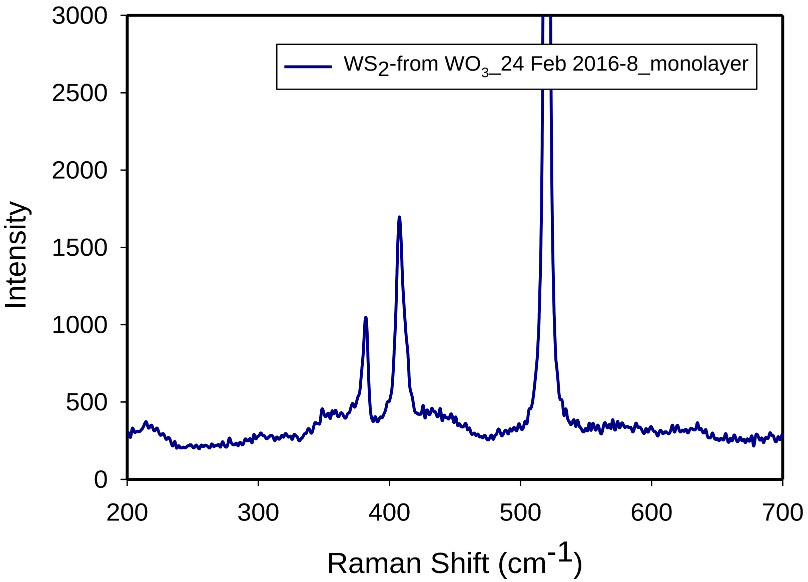
PL



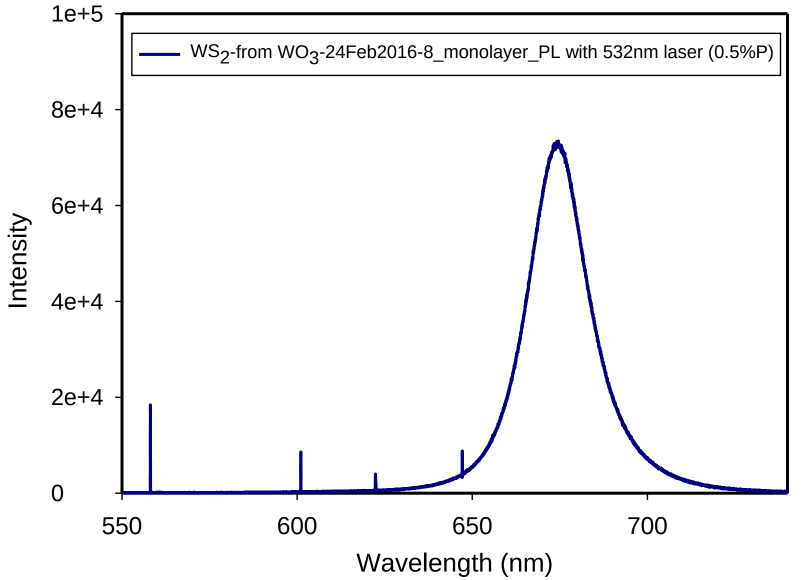
WS_2 / MoS_2 Heterostructures



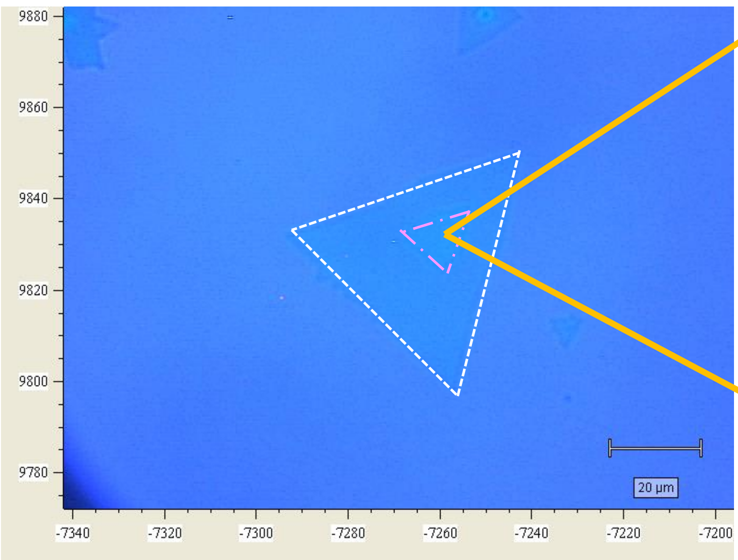
Raman



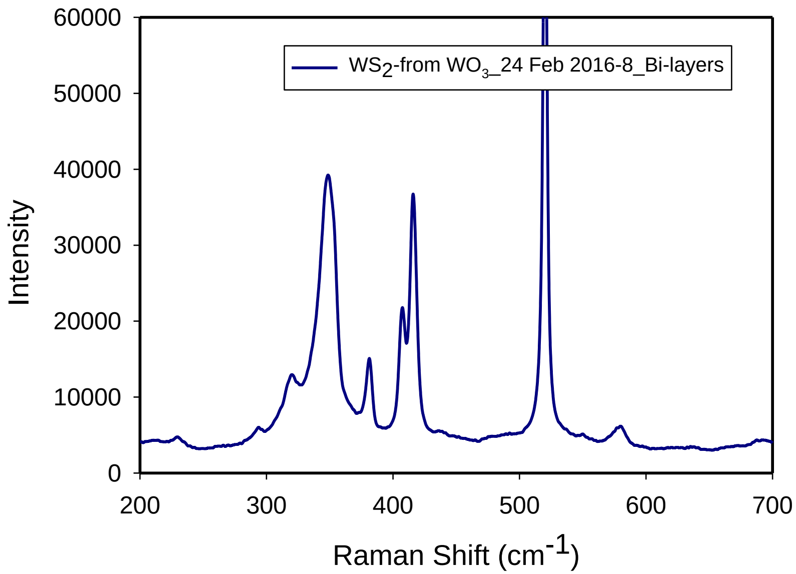
PL



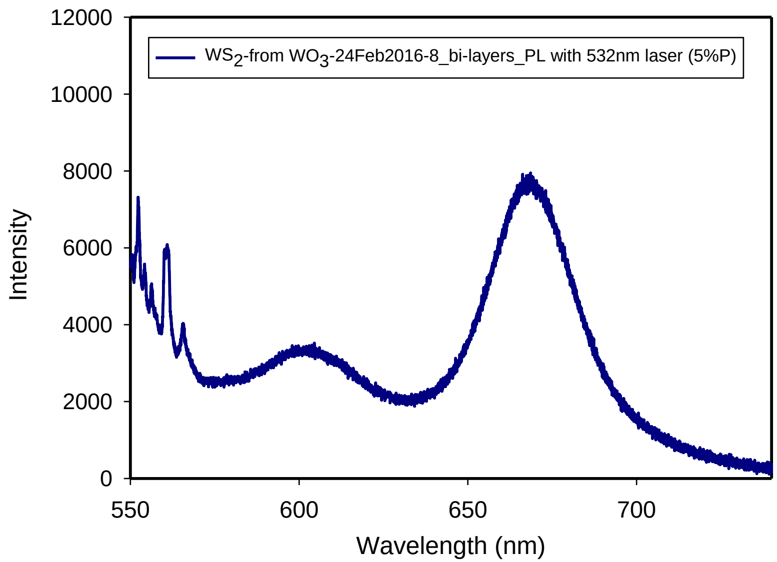
WS_2 / MoS_2 Heterostructures



Raman



PL



Summary:

- A wide range of chalcogenide and 2D materials have been developed by the CVD techniques for emerging applications.
- Wafer scale 2D materials such as graphene, MoS_2, and WS_2 thin films have been successfully fabricated by CVD process which is scalable and can be easily incorporated with conventional lithography.
- Large area 2D materials, such as graphene, MoS_2, and WS_2 thin films transfer technique has been developed with these materials supply to collaborators worldwide.
- Graphene/MoS_2 flakes heterostructures have been developed with the transfer technique.
- CVD processes for monolayer MoS_2 and WS_2 single crystals and MoS_2 / WS_2 heterostructures have been developed.
- Commercialization of 2D materials is on the way.

Collaborators:

Country	Institution	Contacts	Materials
Singapore	Nanyang Technological University	Prof. ZeXiang Shen, Prof. Qing Zhang, Prof. Qijie Wang, Prof. ZhiHeng Loh	MoS2, WS2
Singapore	SUTD/MIT	Prof. Rob Simpson	MoS2, WS2
Hong Kong	Hong Kong Polytechnic University	Dr. Peter Tsang	MoS2, WS2
Taiwan	National Chiao Tung University	Prof. Tsung Sheng Kao, Prof. Hao-chung Kuo	MoS2, WS2
China	Beijing Jiaotong University	Prof. Shuqin Lou	2D materials
China	Shanghai Jiaotong University	Prof. Lina Chi	TiO2
Greece	National Technical University of Athens	Prof. Ioanna Zergioti (with RWE)	2D materials
USA	MIT/Delaware	Prof. Jue Jun Hu	Graphene, Ge-Sb-S
Japan/UK	JAIST/ECS	Prof. Hiroshi Mizuta	Graphene
UK	University of Bristol	Prof. John Rarity, Dr. Daniel Ho	GeSbS, SnS, ZnSe, WS2, MoS2
UK/Brazil	University of Nottingham, Universidade Federal de São Carlos (UFSCAR), Instituto de Física - Universidade de Brasília	Prof Mohamed Henini, Prof Yara Galvão Gobato, Prof Jorlandio Francisco Felix	MoS2, WS2
UK	UoS, Engineering and the Environment	Dr. Zheng Jiang, Dr. Shuncai Wang, Dr. John Walker, Dr. Monica Ratoi	Bi-O-X, TiO2, SnS, MoS2, WS2
UK	UoS, Physics	Prof. David Smith, Dr. Christos Grivas, Prof. Pavlos Lagoudakis	WS2, graphene, MoS2
UK	UoS, ECS	Prof. Harold Chong, Dr. Yoshishige Tsuchiya, Prof. Shinichi Saito, Prof. Themis Prodromakis, Prof. Hywel Morgan	MoS2, graphene, WS2
UK	UoS, ORC	Dr. Bill Brocklesby, Dr Goran Mashanovich, Prof. Anna Peacock, Dr. Pier Sazio, Dr. Sakellaris Mailis, Dr. Nikitas Papasimakis, Prof. Jayanta Sahu, Prof. Rob Eason…etc	Graphene, MoS2, Ge-Sb-S, WS2, 2D materials
UK	Industrials	Oxford Instruments, Plastic logic, Seagate, Artiman, Merck	MoS2, 2D materials

Grants:

	Grants	Valve (£)
1	EP/H02607X/1, EPSRC Centre for Innovative Manufacturing in Photonics (ORC)	£5,125,642
2	EP/M008487/1, Chalcogenide Photonic Technologies (Bristol/ORC)	£594,605
3	EP/N510063/1, Nanomaterials for Smart Data Storage (Seagate/Ilika/ORC)	£211,227
4	EP/N00762X/1, National Hub in High Value Photonic Manufacturing (Shefield, ORC)	£10,220,725
5	EP/M015173/1, Wearable and flexible technologies enabled by advanced thin-film manufacture and metrology (Oxford, Exeter, ORC)	£2,476,881
6	EP/M015130/1, Manufacturing and Application of Next Generation Chalcogenides	£2,508,176
7	EP/N020278/1, Development and Application of Non-Equilibrium Doping in Amorphous Chalcogenides	£261,632
	Total	£21,398,888