Transmission electron microscopy
for atomic scale investigation of 2D materials

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LEMMA @ Nano-characterization platform (PFNC)

Atom probe
TEM (7)
SEM (5)
FIB (4)

INAC/LETI/LITEN

MEIS

Nano & micro electronics
Optic
Spintronics & magnetism
New energy
Biology
2D materials
OUTLINE

✓ What is two-dimensional materials?

✓ Atomic scale investigation for 2D materials

✓ Low-Voltage Aberration Corrected TEM

✓ Use of TEM techniques for 2D material study
  - Defect & Grain boundary analysis
  - Single atom detection
  - Dynamic study
  - Application to Transition Metal Dichalcogenides

✓ Conclusions
### What is “two-dimensional (2D) material”?

<table>
<thead>
<tr>
<th>0D</th>
<th>1D</th>
<th>2D</th>
<th>3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atoms</td>
<td>Nanotubes</td>
<td>Atomically thin layer</td>
<td>Bulk</td>
</tr>
<tr>
<td>Quantum dots</td>
<td>Nanowires</td>
<td></td>
<td></td>
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<tr>
<td>Nanoparticles</td>
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</tbody>
</table>

**CARBON ALLOTROPES**

- **Fullerene**
- **Nanotubes**
- **Graphene**
- **Diamond**
- **Graphite**

**Nobel Prize in 1996**

- Smalley & Kroto

**Carbyne**
First true 2D materials

**Graphene fundamental has been studied**
- Theoretical approach
- Experiments on model systems

**First true 2D material = GRAPHENE**

- **Electronic property**: zero gap semiconductor
- **Ultra strong**: 45N/m, > 100 times stronger than steel
- **Electron mobility**: 200 000 cm²/Vs (theo.)
- **Conductivity**: Better than copper (theo.)
- **Optical transparent**: absorbs only 2.3%
- **Thermal conductivity**: conducts heat 10 times better than Ag at RT

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**Nobel Prize in Physics 2010**

**Novoselov and Geim**

*Science 2004* **306** p666
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**Chemical Vapor Deposition**

**Nobel Prize in Physics 2010**

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**Arrival of other 2D materials:**
- BN, Transition Metal Dichalcogenides (TMDs)

**New 2D materials:** MoS₂, WS₂, MoSe₂, etc...

**Semiconducting materials**: 1L: Direct band gap
Atomic structures of 2D materials

Is visualization of atomic structure possible?

“Grain boundaries in polycrystalline materials may alter the electronic properties.”

Atomic configuration in mono atomic layer can modify physical properties

Magnetic property in graphene

an effective way to tailor the render its potential use for


Kondo effect: University of Maryland
Transmission Electron Microscopy (TEM)
Atomic Resolution Imaging

**High resolution image of Si grain boundary**
@ 400kV JEOL in 2003  JL Rouviere

Higher acceleration voltage
→ higher spatial resolution
Transmission Electron Microscopy for **Graphene**

- Physical properties of graphene directly depend on atomic structure
- Damage free observation → low voltage → **low resolution**
- Few interaction with single atomic layer → **low signal**

- Spatial resolution @ low voltage
- Sample preparation
- Contamination
- Electrical & mechanical Stability
- Optimization of parameters
Invention of aberration corrector!
Transmission Electron Microscopy for **Graphene**

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*Titan\(^3\) Ultimate (FEI)*

Graphene grown by V. Bouchiat (Néel)
2D materials study using TEM techniques
Defect structure in graphene

Simulated image
Atomic model

Atomic position determination
of vacancies in monolayer graphene

Coll. V. Bouchiat (Néel) & G. Cunge (LTM)
Defect structure in graphene

Defect structures

Graphene grown by J. Dijon (LITEN)

BigDFT calculations (Pascal Pochet, INAC): 448 atoms, Γ point; formation energy wrt pristine graphene

Defect structures with DFT calculation → Formation study
Most of synthesized graphene layers are polycrystalline...

Model of polycrystalline graphene

How can we get grain information in continuous monolayer?

Graphene grown by A. Tyurnina (LITEN)

Mortazavi et al. Nanoscale (2014)
Grains in monolayer graphene?

Grain size and grain boundaries are keys for graphene properties

Multi-scale analysis is one of advantages in TEM

→ Grain size distribution and related rotation angle can be identified in large area
Grain size & grain boundaries?

Raman study of CVD grown graphene

Raman spectroscopy
Powerful technique to know:

✓ Presence & degree of defects
✓ Mean grain size
✓ Number of layers etc...


Grain size & grain boundaries?

Raman study of CVD grown graphene

Grain size evolution visualized by TEM

Impurity atoms in graphene layer

Impurity atom detection: Si atoms

Graphene layer contains a lot of Si contamination

Filtered images

Coll. V. Bouchiat (Néel) & G. Cuneg (LTM)
Single light atom detection

**Light atom detection: N atoms**

**TEM imaging beyond structural information**

Associating with an image simulation using DFT model, the charge distribution around N atoms incorporated in graphene network is identified in an atomic TEM image.

*J. C. Meyer et al. Nature Mater. 10 (2011) 209*
Direct observation: dynamic study

*Electron beam irradiation can be used as a driving force to modify the atomic structures of 2D materials*

→ Direct observation
→ Formation and evolution of defect structures

*Formation of covalent bonding between fullerene & CNT wall*
Direct observation: dynamic study

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**Formation of covalent bonding between fullerene & CNT wall**

**Formation of Carbyne**

1D carbon structure

H. Okuno
For further analysis... Scanning TEM
**STEM imaging: Z-contrast**

Contrast $\propto Z^2$ (Z: atomic number)

**Sample: GaN quantum dot in AlN**

Non-doped

Structural information + chemical contrast

*Sample thickness 5 – 10 nm = 32 to 64 atom thick*
**Single atom detection & EELS Spectroscopy**

**STEM imaging + Electron Energy Loss Spectroscopy (EELS)**
- Identification of Si atoms by Z-contrast
- EELS spectroscopy reveals chemical bonding on each single atoms

Intensity $\propto Z^\alpha (Z_C=6, Z_{Si}=14)$

Extremely difficult: Contamination during spectrum acquisition, damage (atom movement) etc.
→ Still limited to highly sophisticated equipment...

60kV
Interface analysis in Van der Waals heterostructures

**Growth of vertical and lateral Van der Waals heterostructures**

\[ \text{Intensity} \propto Z^\alpha \quad (Z_{Mo} = 42, Z_{W} = 74) \]

“The fabrication of 2D heterostructures with clean and sharp interfaces, essential for preserving optoelectronic properties driven interlayer or intralayer coupling remains challenging”

A. Geim et al. Nature 499 (2013) 419425

**Lateral heterostructure**

Direct observation: Phase transition in TMD monolayers

“We discover that mechanical deformations provide a route to switching thermodynamic stability between a semiconducting and metallic crystal structure”

Direct observation: Phase transition in TMD monolayers

Atomic mechanism of the semiconducting-to-metallic phase transition in single-layered MoS$_2$

Yung-Chang Lin, Dumitru O. Dumenco, Ying-Sheng Huang and Kazu Suenaga

Suenaga’s team Nature Nanotechnol. (2014)

Control and direct observation of phase transition ‘semiconductor’ to ‘metallic’
- Electron beam is driving force applied inside TEM
- Direct observation of detailed atomic structure
- Study the energy & mechanism of phase transition
Conclusions

✓ Low-voltage aberration corrected TEM imaging provides precise information on local structures of atomically thin 2D materials down to atomic scale @ 80kV

✓ Controlling various aberrations, such as spherical aberrations, and defocus, we can determine the atom positions in monolayer graphene by TEM imaging. Vacancies, Defects, Grain boundaries, Dopant are possible to visualize

✓ Electron beam can be used to move atoms, dynamic study by direct observation is possible. Formation of defects, phase transitions

✓ STEM imaging provides local chemical information, EELS spectroscopy identify the chemical elements & chemical bonding
Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) are powerful tools for studying 2D materials. TEM is used for imaging defects and grain boundaries, while STEM is particularly useful for single atom detection and chemical contrast, where the intensity is proportional to the atomic number ($I \propto Z^2$).

**Defects & grain boundaries**

- MoSe$_2$
- Graphene

**Migration of defects**

Dynamic study under the electron beam.

**Substitution & Hetero structures**

Challenges in LEMMA

**Thickness measurements**

**Diffraction**

- EELS
- WS$_2$
- Mo$_2$S$_4$
- CEA: Coll. Liten
- CEA: Coll. Néel
- CEA: Coll. M. Jamet & A. Marty
- CEA-Grenoble: Thesis of Y. Martin 2014

Pennycook et al. PRL 2012

Gong et al. Nature Materials 2014

CEA: Coll. Liten

CEA: Coll. M. Jamet & A. Marty
Thank you

Jean Dijon (LITEN/CEA)
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Gilles Cunge (LTM/CNRS)
Yannick Martin (INAC/CEA)
Matthieu Jamet (INAC/CEA)
From **basic** to **applied** research

A multi-department consortium devoted to:

1) **property-driven materials identification and growth**

2) **materials and devices up-scaling**

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