Nanoscale Thermal Measurements -- New Challenges and New Opportunities

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Aug. 14, 2023

What is heat?


Aristotle, 384-322 BC   Lavoisier， 1743-1794

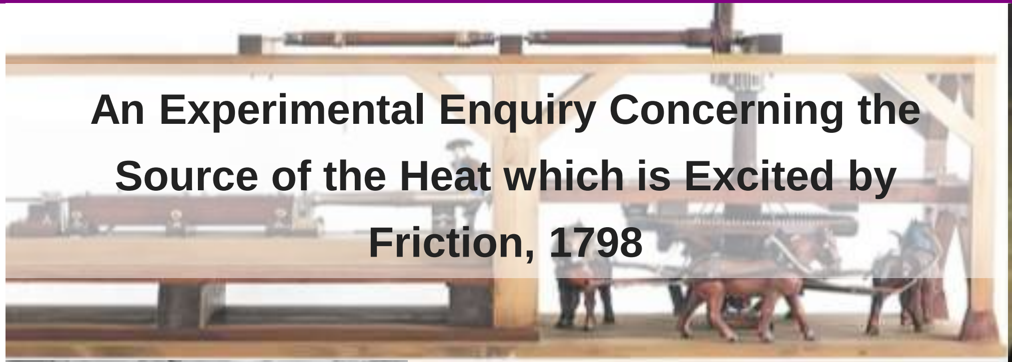
Heat is a hypothetical weightless fluid known as caloric.


Bacon, 1561-1626   Hooke, 1635-1703

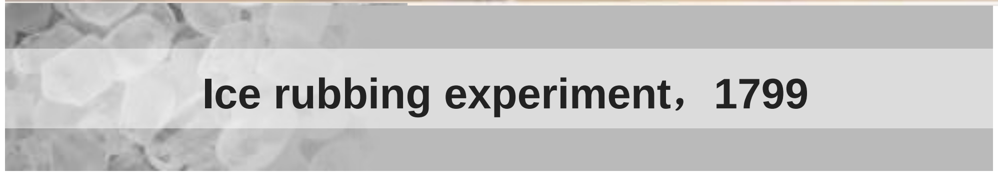
Heat is not a substance but is a matter of motion.

Caloric Theory → Heat？ ← Kinetic Theory

Experiments and measurements —— dispute resolution



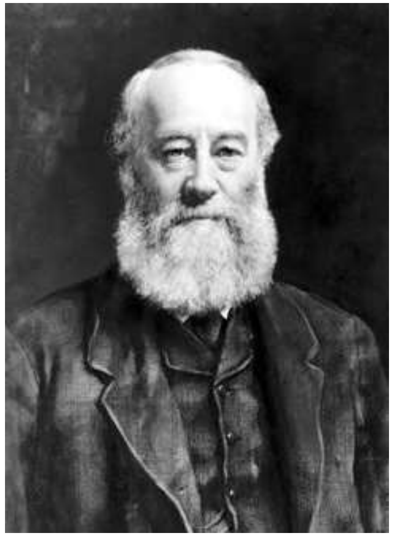
An Experimental Enquiry Concerning the Source of the Heat which is Excited by Friction, 1798



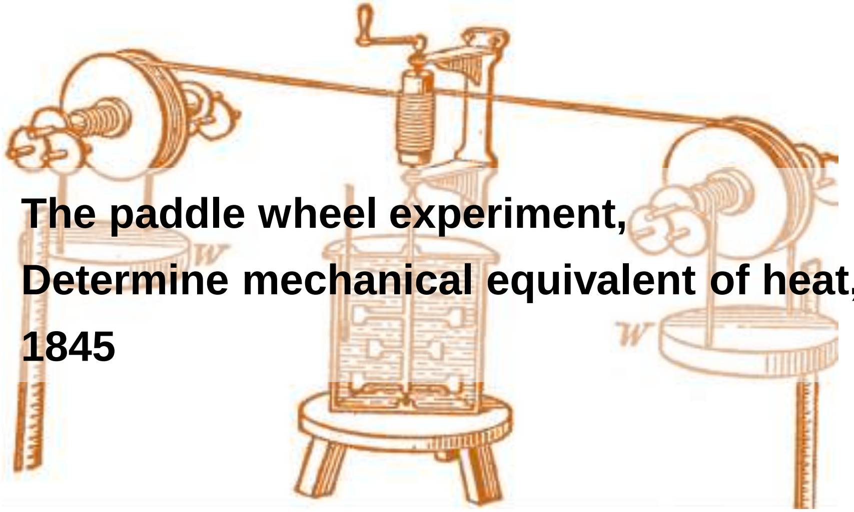
Ice rubbing experiment，1799

Benjamin Thompson(Rumford)
1753-1814

Humphry Davy
1778-1829



James Prescott Joule, 1818-1889



The paddle wheel experiment,
Determine mechanical equivalent of heat,
1845

- **Prove the Kinetic Theory**
- **Propose the Law of Conservation of Energy**

Experiments and measurements
—— discovery new phenomenon and conjectures

Baron Jean Baptiste Joseph Fourier
1768-1830

Fourier Law of Heat Conduction

$$\boxed{q = -\lambda \frac{dT}{dx}}$$

The Analytical Theory of Heat

1822

- Summarized from thousands of experiment results
- Which still guides heat transfer research today
- Become the fundamental of Heat Transfer Research

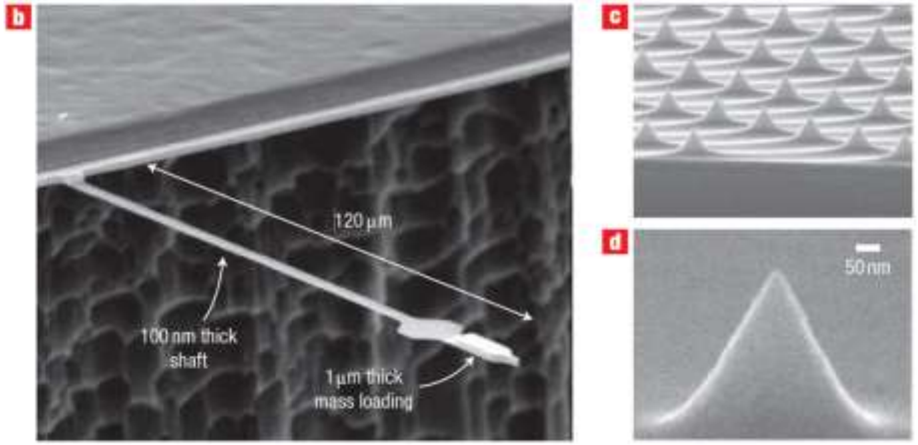
Important approaches in thermal science

Experiments and **measurements** have become important approaches in thermal science research,

especially for **new phenomena**, **new concepts**, and **new technical challenges**.

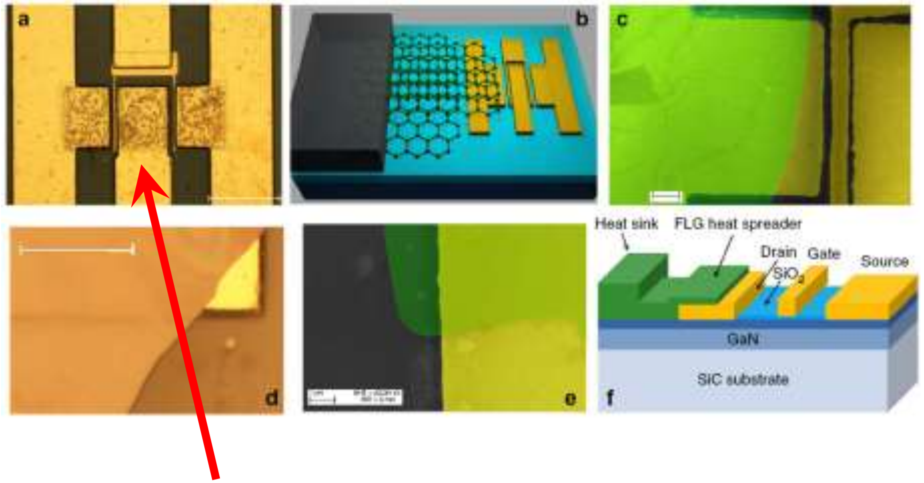
Background

- **Nanotechnology has started a new revolution of fabricating, measuring and manipulating materials on nanometer levels.**



Magnetic resonance force microscopy nanosensor

Nature nanotechnology, 2007

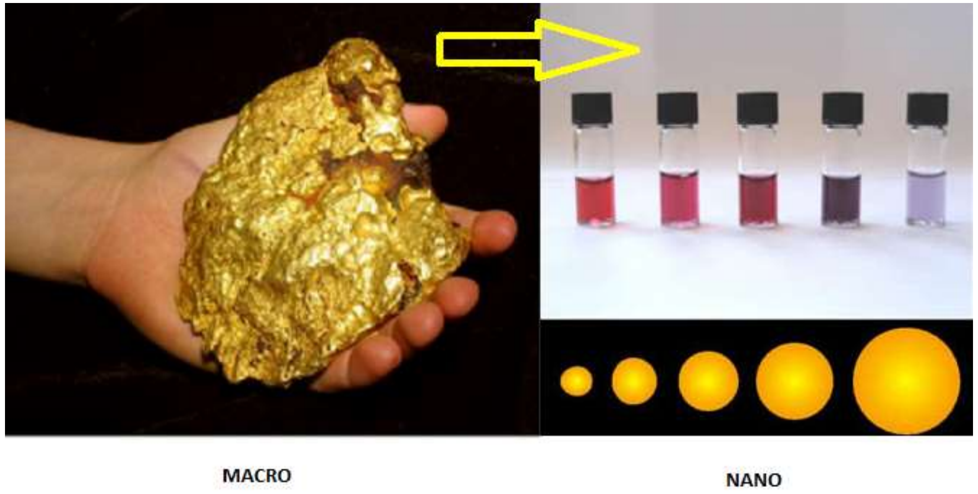


Graphene based heat spreader for cooling high power transistors

Nature communications, 2012

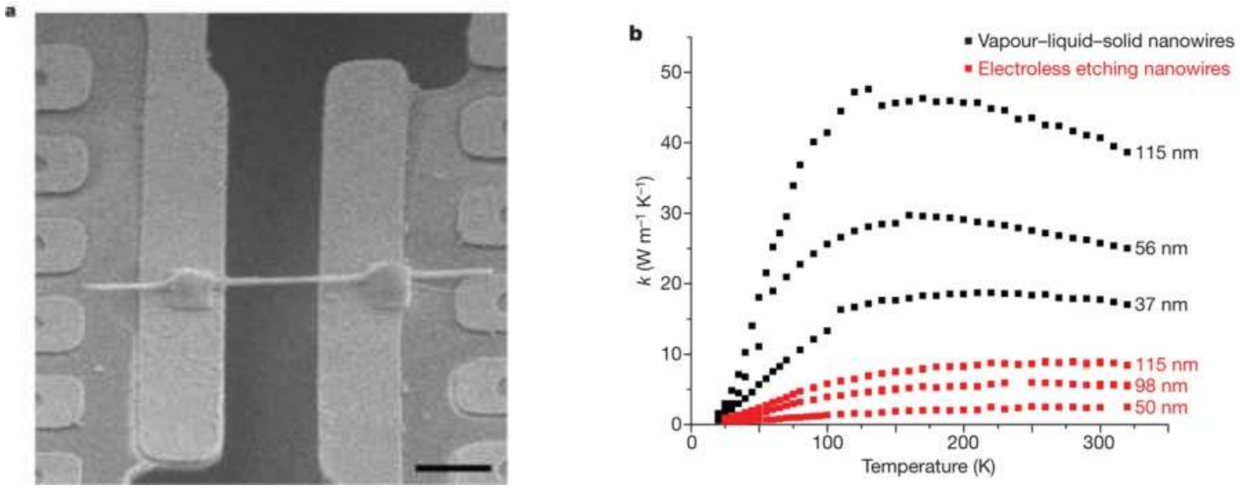
Background

At nanoscale, gold does not look even yellow!



http://blog.manuscriptedit.com/2014/01/size-matter-nano-vs-macroscopic-world/

Thermal conductivity of Si nanowire greatly decreases



Hochbaum et al. ***Nature* 451**, 163-167, 2007

- **Nanomaterials are called size matters, must measure!**

TPMs at Nanoscale are very difficult!

Part I

Contact measurement methods for nanoscale materials

Part II

Non-contact measurement methods for nanoscale materials

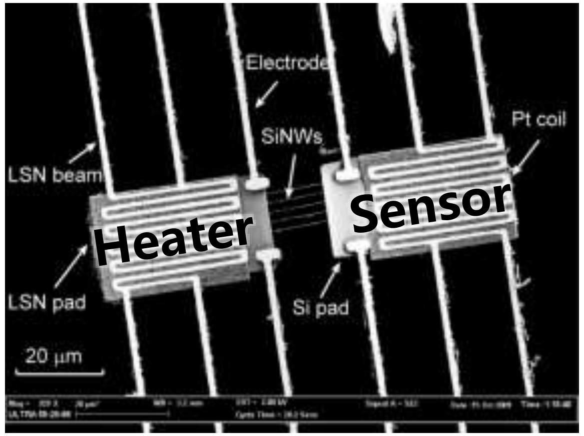
Part III

Expand applications in Multidisciplinary Research

Nanoscale measurement methods

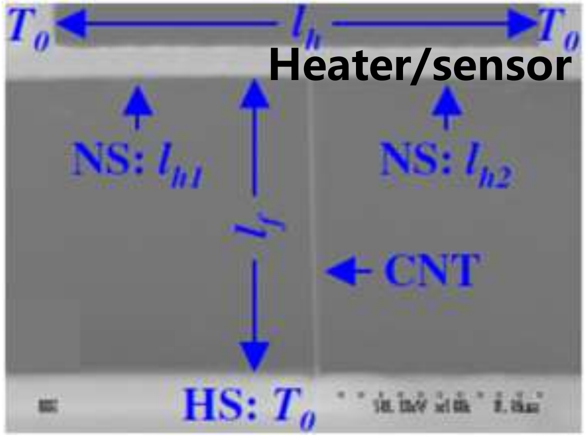
➢ For contact methods

Microfabricated suspended device method



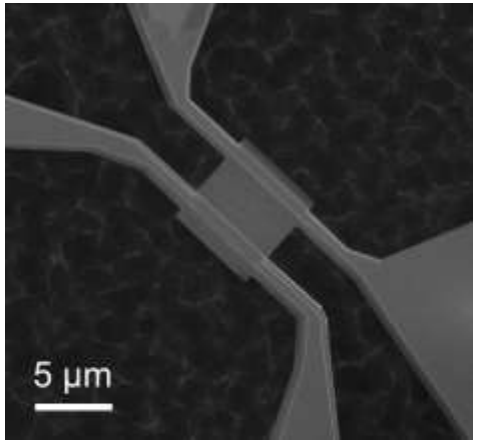
Majumdar A *et al. J. Heat Transf.* 2003
(University of California, Berkeley)

T type method



Zhang X *et al. Phys. Rev. Lett.* 2005

H type method



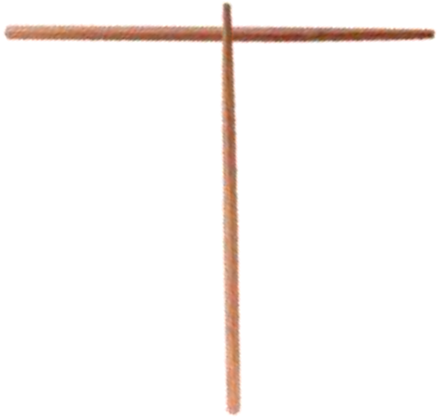
Zhang X *et al. Science.* 2022

- Classic contact methods, such as the hot wire method and the 3ω method, were not really adequate for nanomaterials such as CNT
- New nanoscale thermal measurement techniques were successively developed around the turn of the century
- High temperature resolution and high measurement sensitivity

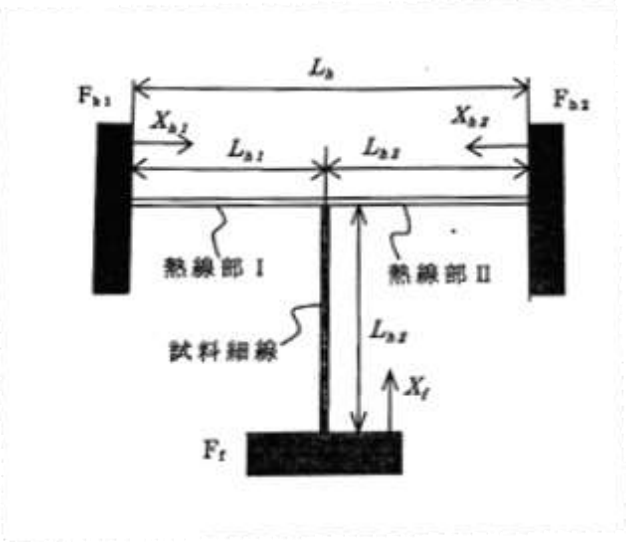
T-type method (proposed in 1998)

- The T-type method for micro/nanowires was developed in 1998

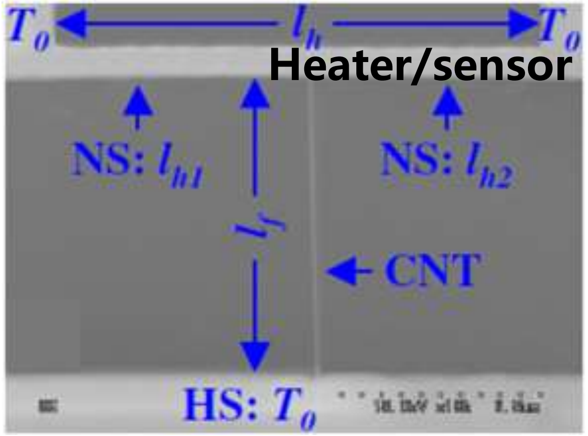
Inspiration source:



Chopsticks



Model of T-type method

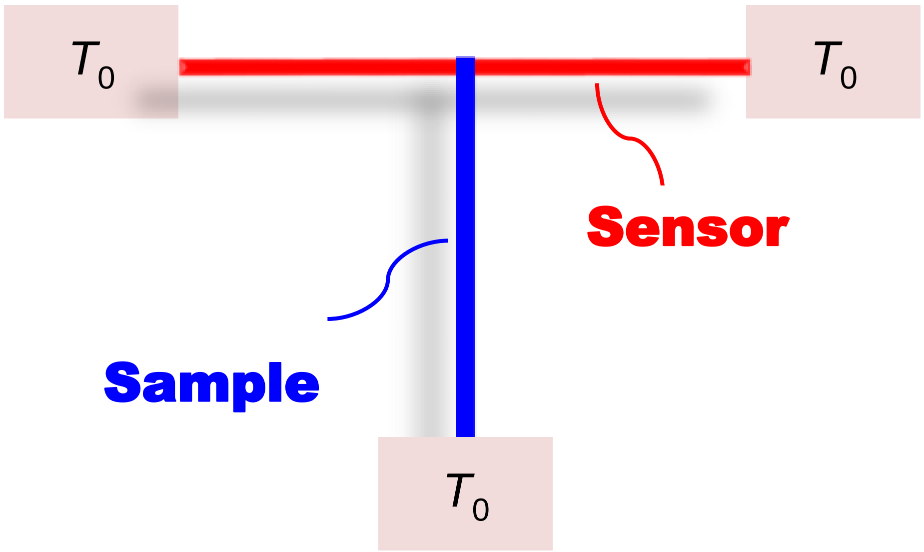


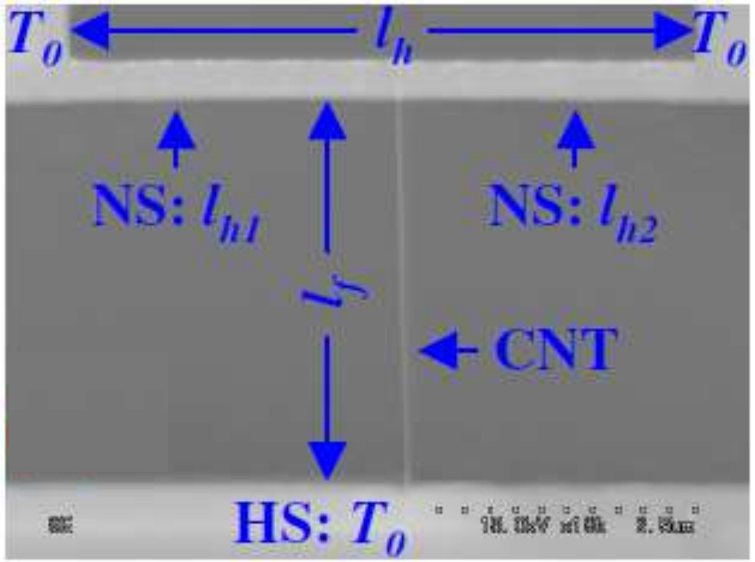
Zhang X *et al. Phys. Rev. Lett.* 2005

- In 2005, Zhang et al. determined the thermal conductivity of an individual multi-walled CNT by the T-type method
- Discussed the thermal contact resistance influence in CNT measurement for the first time
- Analyzed the definition of the cross-sectional area of CNT

Principle of T-type method

- T-type connection between the sensor and sample

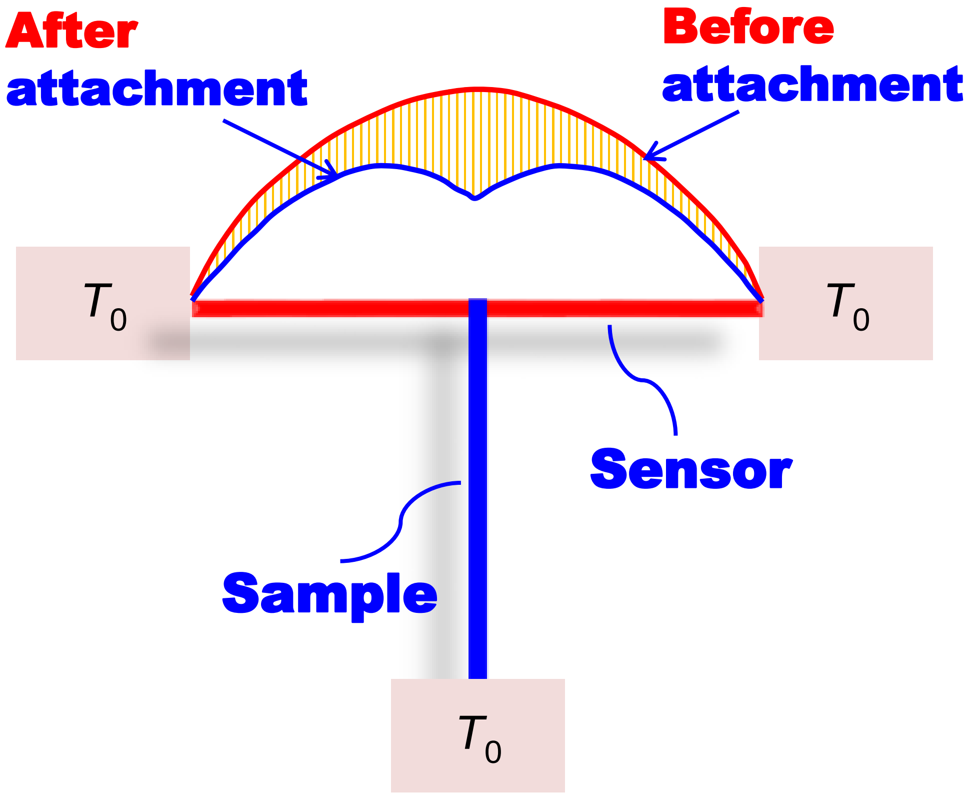


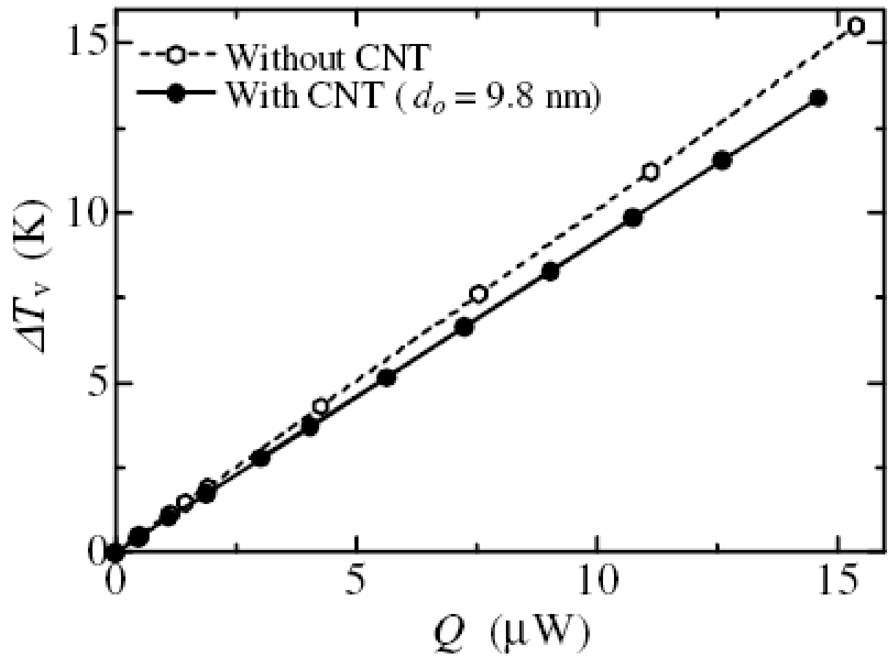


Suspended sensor:

- ➢Heater
- ➢Heat flux meter
- ➢ Resistance thermometer
- ➢ Conductor

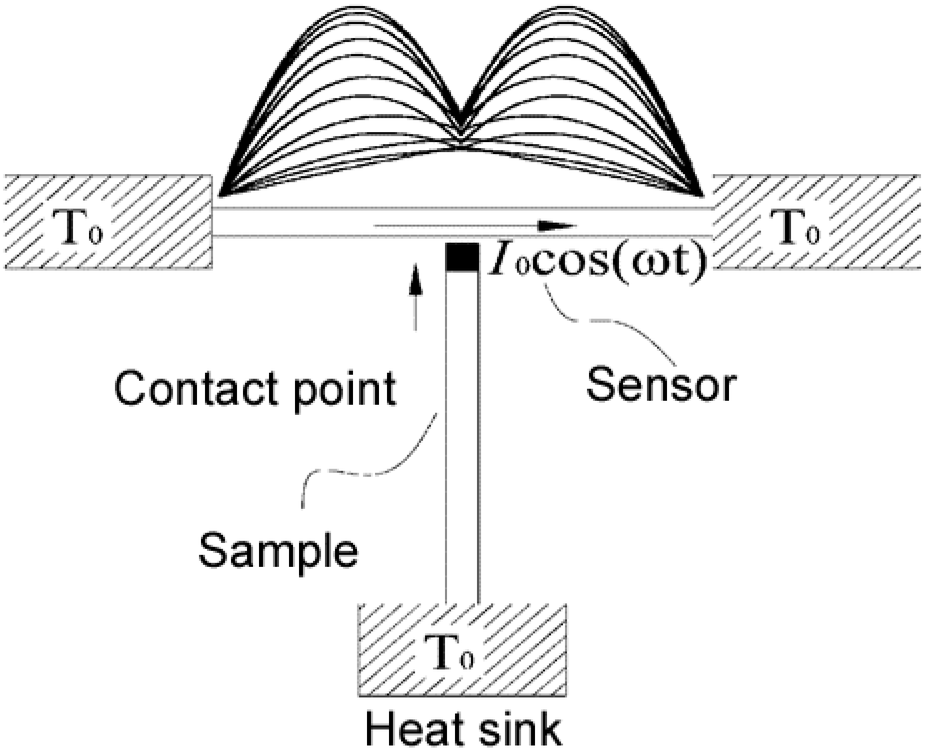
DC heating-DC detecting T type method for thermal conductivity measurement

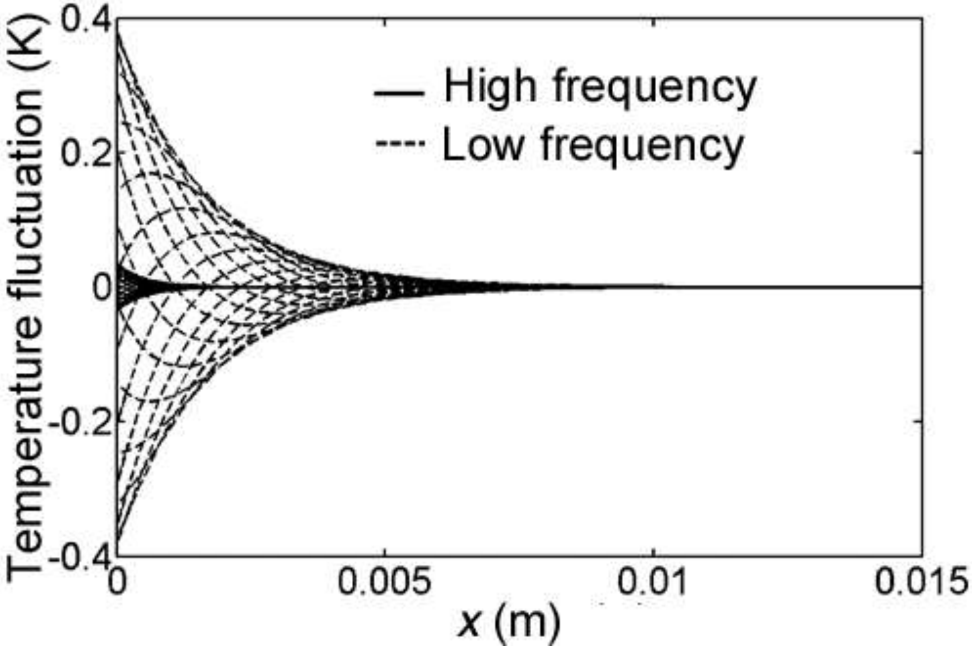




The thermal conductivity can be extracted from comparing the average temperature change of the hot wire without and with the attached sample for a given dc heating current.

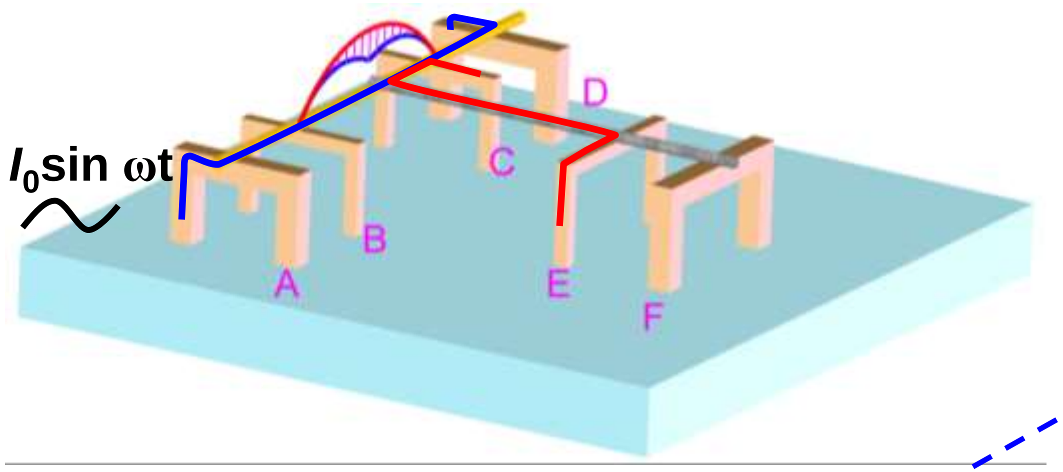
Measure the thermal effusivity and thermal contact resistance using 3ω-T type method

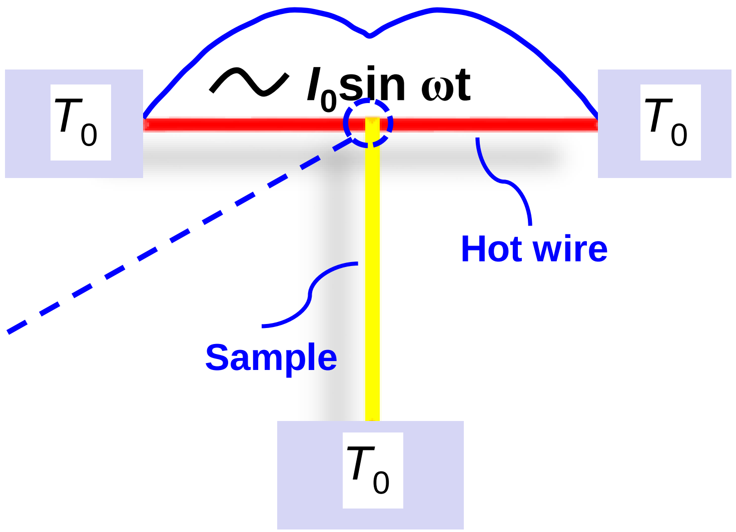


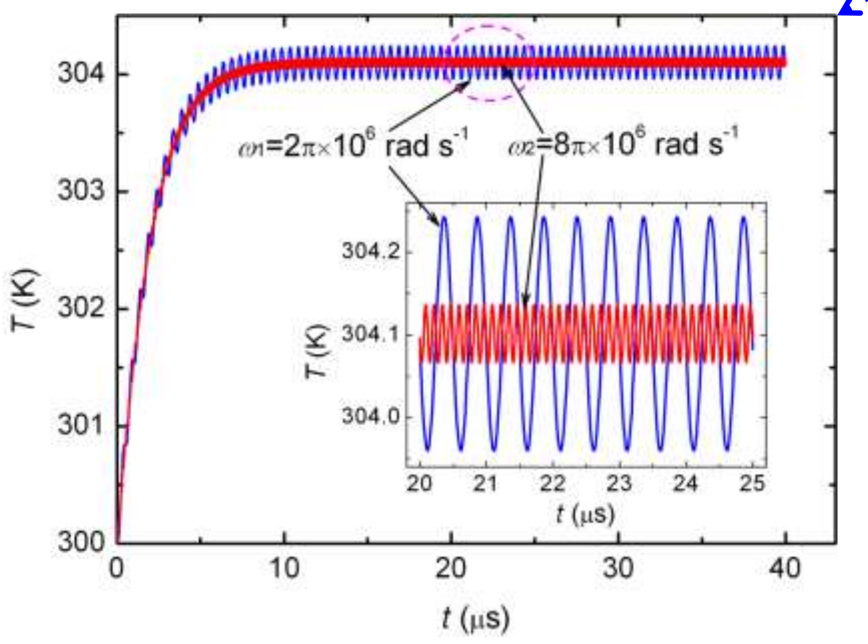


To adjust the thermal penetration depth axially by adjusting the frequency of the heating current.

Seebeck coefficient - AC heating-DC detecting







$$\Delta T_f = \Delta T_{f,static} + \Delta T_{f,harmonic}(t)$$

$$\Delta T_{f,static} = \frac{I_0^2 R_h l_{h,1} l_{h,2} l_f}{4\left(A_f \lambda_f l_{h,1} l_{h,2} + l_f A_h \lambda_h l_h\right)}$$

$$V_s = S \cdot \Delta T_{f,static}$$

Measurement principle

T-type method	Physical properties
◆ Four-probe mode	◆ Electrical conductivity
◆ DC heating-DC detecting mode	◆ Thermal conductivity (Thermal contact resistance affected)
◆ 3ω-T mode	◆ Thermal effusivity, ◆ Thermal contact resistance, ◆ Specific heat
◆ AC heating-DC detecting mode	◆ Seebeck coefficient

Integration

- Electrical conductivity
- Temperature coefficient of resistance

- Thermal conductivity
- Thermal diffusivity
- Specific heat
- Thermal effusivity
- Thermal contact resistance

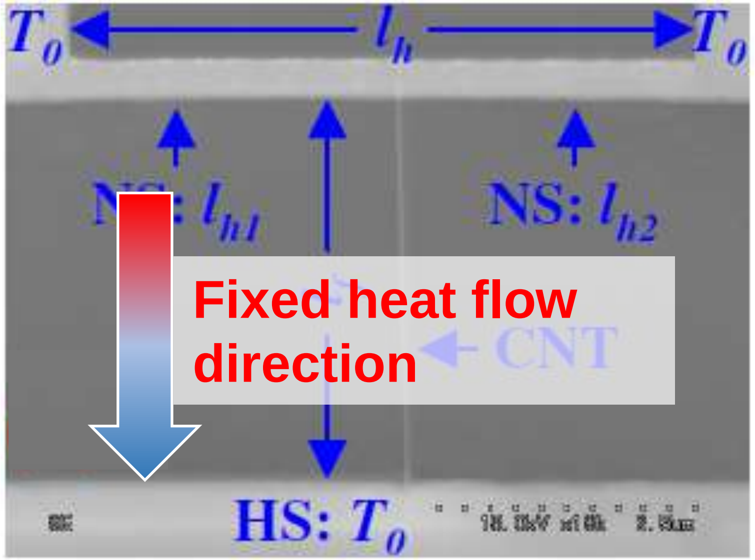
- Seebeck coefficient
- Figure of merit

Photo of T-type Instrument

Limitation of T-type method

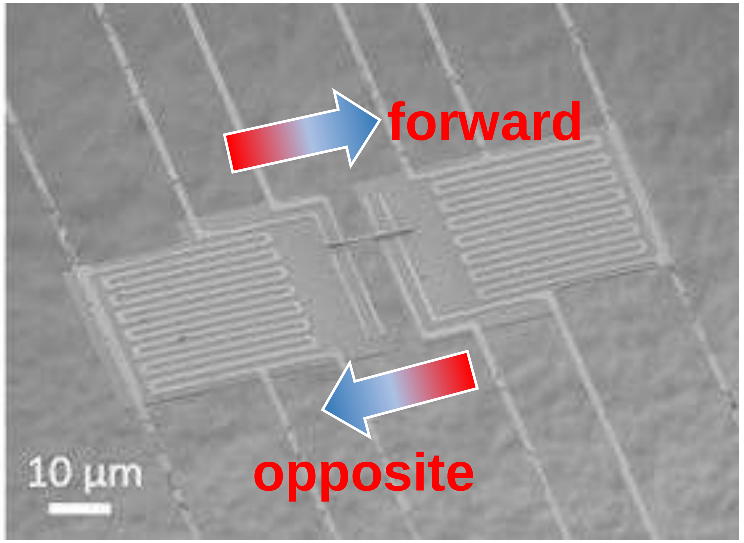
- The direction of heat flow cannot be changed

Single direction: from the hot wire to heat sink



T-type method

Two way: heating island and probing island can be exchanged



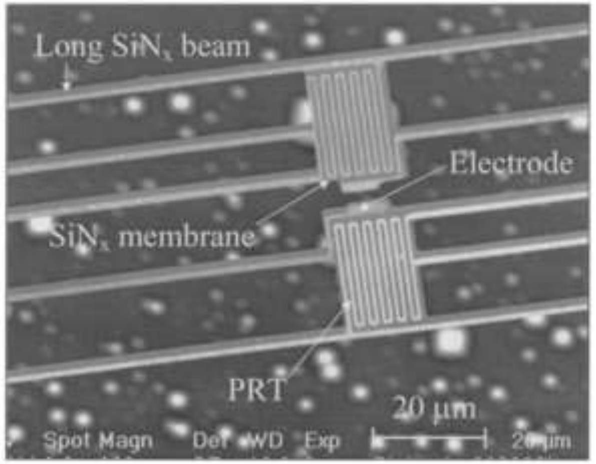
Microfabricated suspended device method

➢ Can be used to study the thermal rectification effect

Microfabricated suspended device method

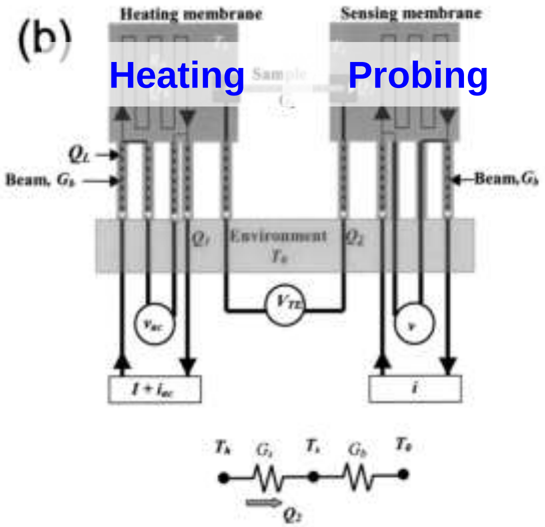
- In 2001, Majumdar et al. developed the microfabricated suspended device (MSD) method for measuring the thermal conductivity of multi-walled CNT
- The thermal conductivity of the sample is obtained from the heating power and the temperature rises of the heating and probing islands at equilibrium
- Simple model with convenient data processing, has a wide range of applications while requiring very sophisticated nanofabrication techniques.

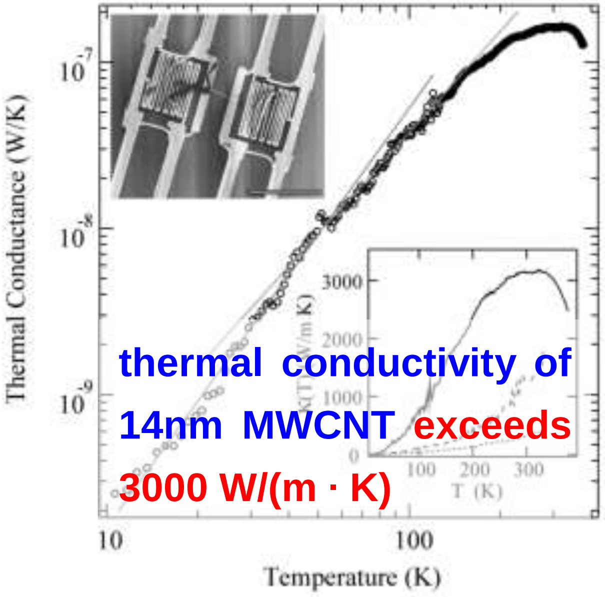
(a)



PRL **87**, 215502 (2001)

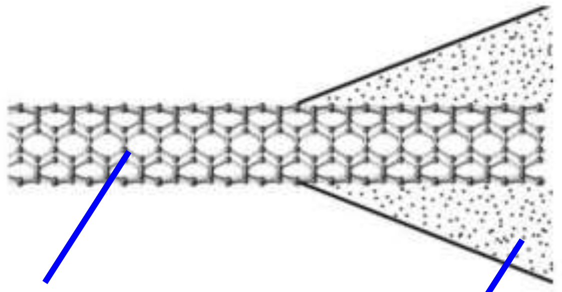
(b)





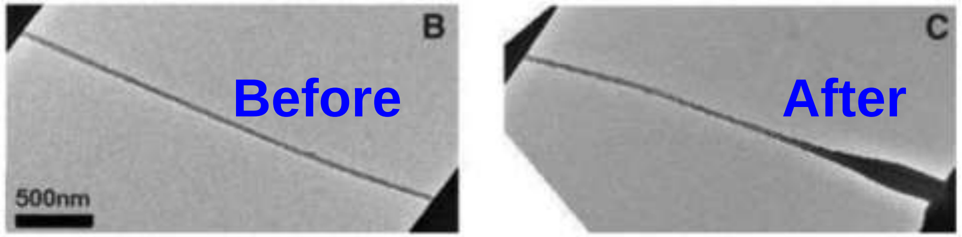
Measurement of thermal Rectification

- **Thermal Rectification：Differences in thermal conductivity in different directions**

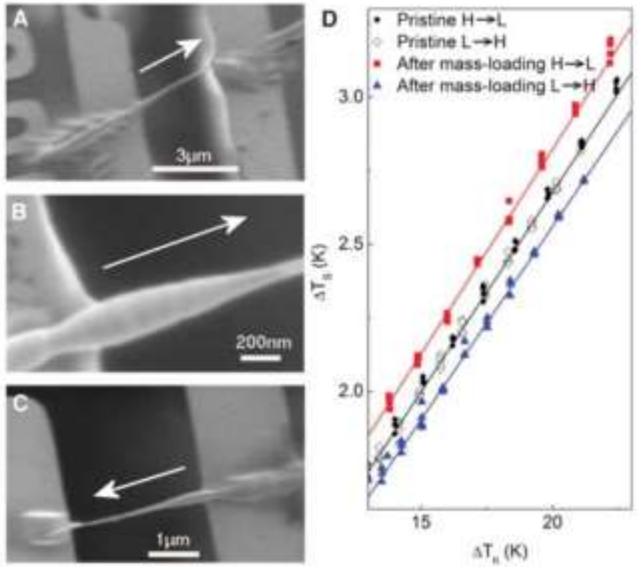


CNT/BNNT

Asymmetric deposition $C_9H_{16}Pt$



Science, **314**, 1121-1124 (2006)



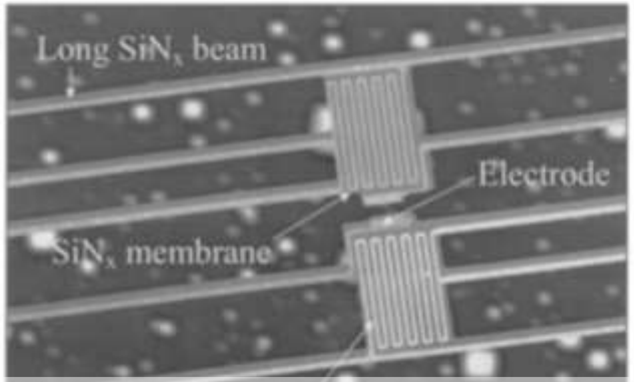
Thermal rectification factor determined by microfabricated suspended device method

- **CNT: 2%**
- **BNNT: 3% -7%**

Is the measurement result reliable?

Limitation: non-ignorable heat radiation

- Island area: 15 μm×20 μm, distance: 2 μm
- SiN_x Cantilever area: 400 μm×3 μm
- thickness: 500 nm
- Radiated emissivity: 0.71
- Experimental condition: room temperature, CNT with a diameter of 14 nm and thermal conductivity of 3000 W/(m·K), temperature difference is 20 K



Microfabricated suspended device method

- Heat flow through carbon nanotubes $$Q_1 = \kappa A \frac{\Delta T}{L} = 4.6 \times 10^{-6} \mathrm{W}$$
- Heat Radiation between the two island $$Q_2 = \varepsilon \sigma A \left(T_h^4 - T_0^4 \right) = 1.1 \times 10^{-7} \mathrm{W} \quad \sim 2\%$$
- Heat Radiation between the islands /cantilever and the environment $$Q_3 = \varepsilon \sigma A \left(T_h^4 - T_0^4 \right) = 3.0 \times 10^{-7} \mathrm{W} \quad \sim 6.5\%$$

The large surface area of the islands makes non-negligible thermal radiation effect and measurement uncertainty for the MSD method

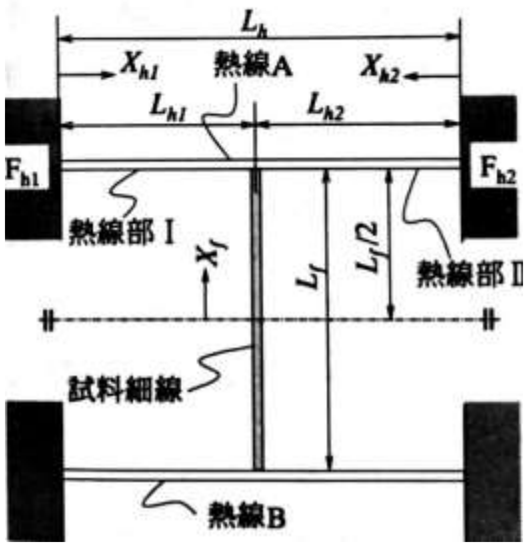
H-type method

- **H-type method** for measuring **the hemispherical emissivity** and **thermal conductivity** of micro/nanowires was proposed **in 1998** (X. Zhang et. al. the same year as the T-type method)

Short-Hot-Wire Method for Measuring Total Hemispherical Emissivity of a Fine Fiber

Seiji FUJIWARA, Xing ZHANG and Motoo FUJII

(November 10, 1998)

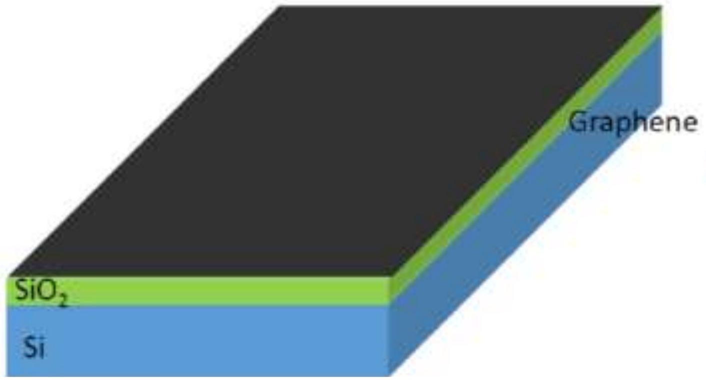


Model of H-type method

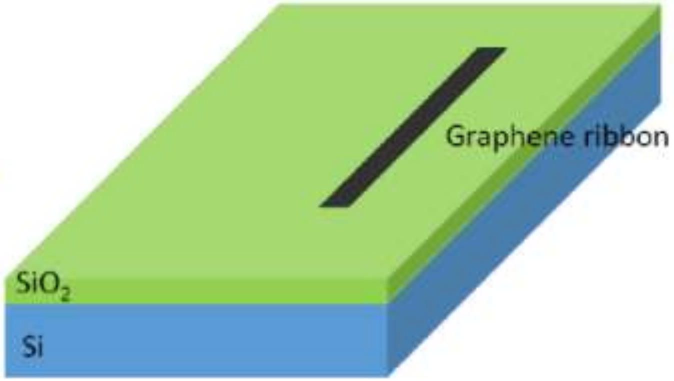
- **Replaces the heat sink** in the T-type method **with another hot wire**
- **Higher sensitivity** and flexibility
- **Less impact of heat radiation**
- Relying on **nanomanufacturing** technology

Integrate manufacture sample and device

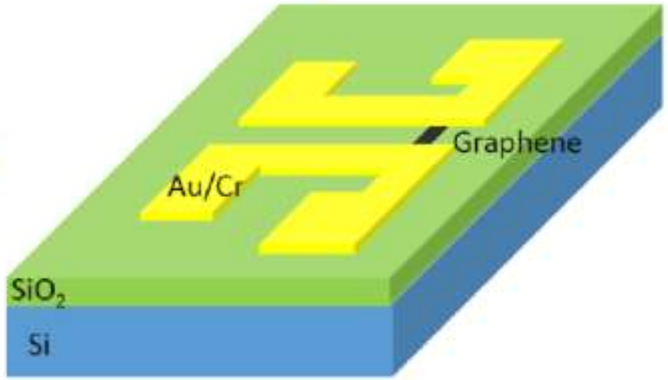
An example of fabricating free-standing large-area single-layer graphene (SLG) membrane



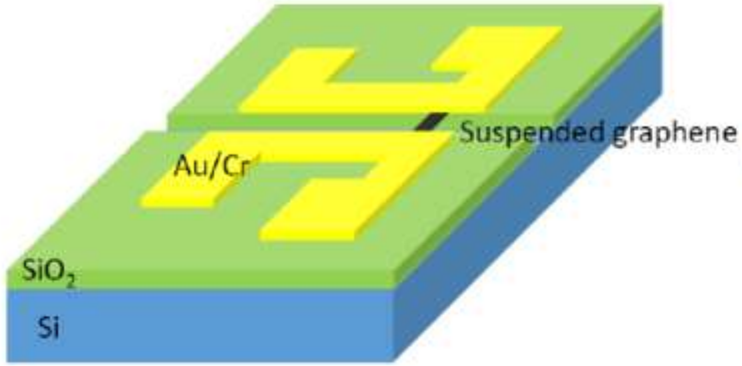
Cu-CVD graphene transferred to Si wafer



EBL+O_2 plasma: patterning graphene nanoribbon



EBL+PVD: Au/Cr electrodes



SiO_2 etched by BHF + critical point dry: suspending ribbon

Suspending large area SLG membrane fabrication

Secondary electron beam lithography

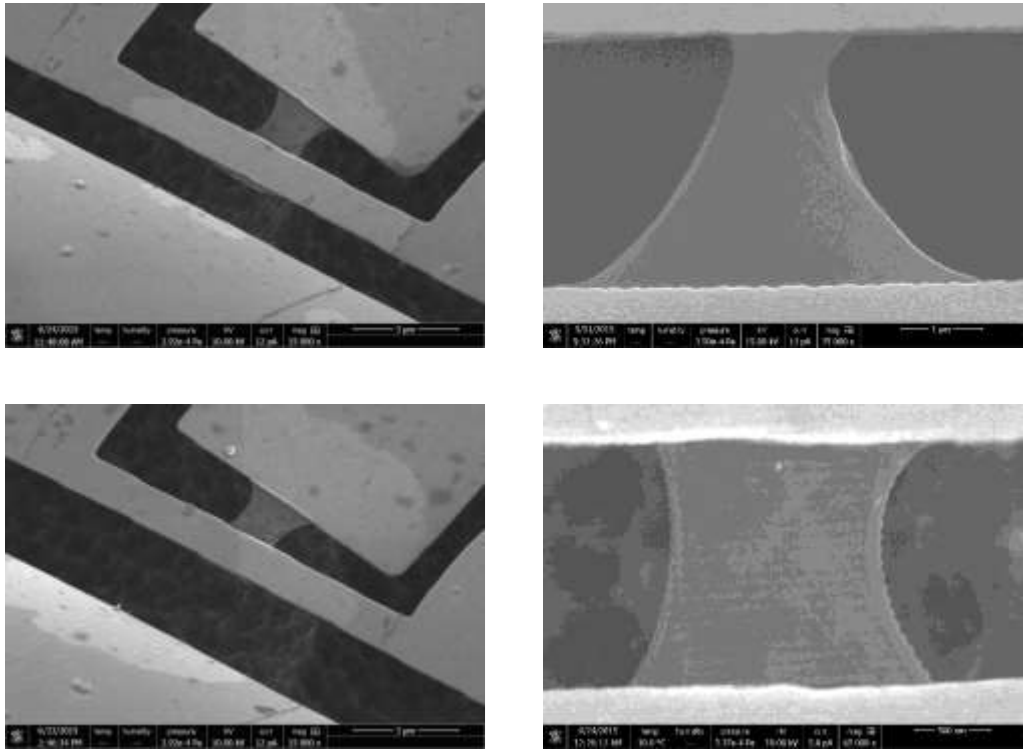
to realize accurate positioning

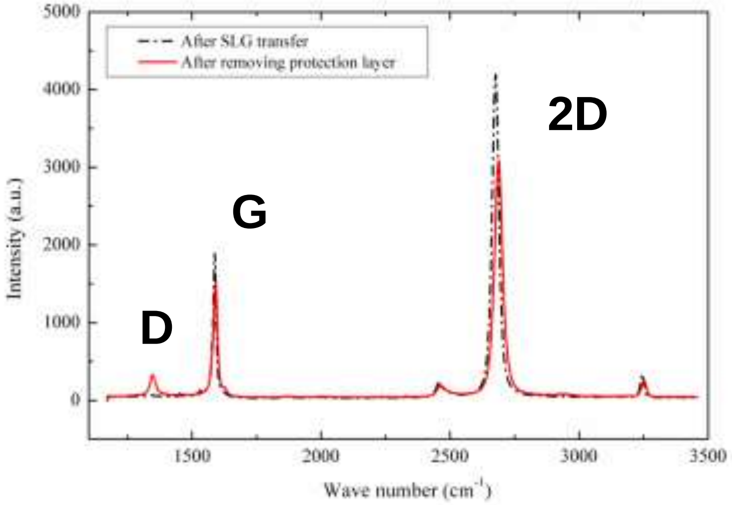
O_2 plasma: **determine the width of fabricated SLG**

Carbon dioxide supercritical dry technique: **to avoid break caused by surface tension**

Suspending large area SLG membrane fabrication

- This method can be applied to lots of 2D materials, includes graphene, MoS_2, etc., and it can fabricate the **large area and high-quality atom-thick sample**.

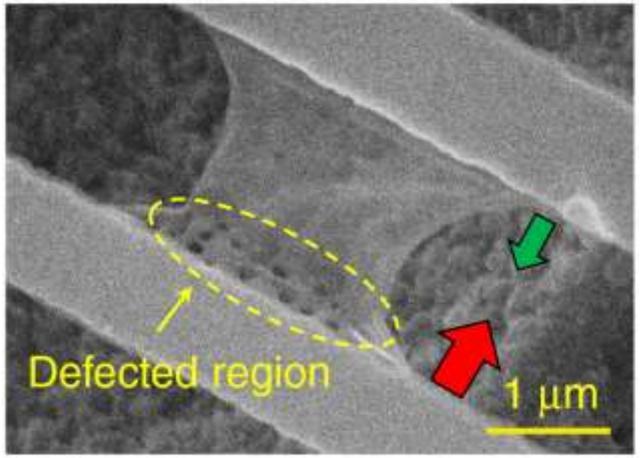


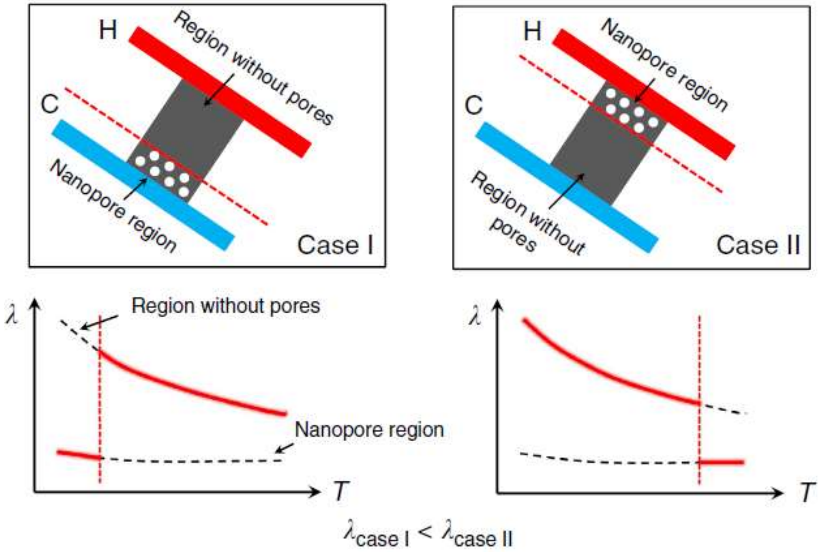


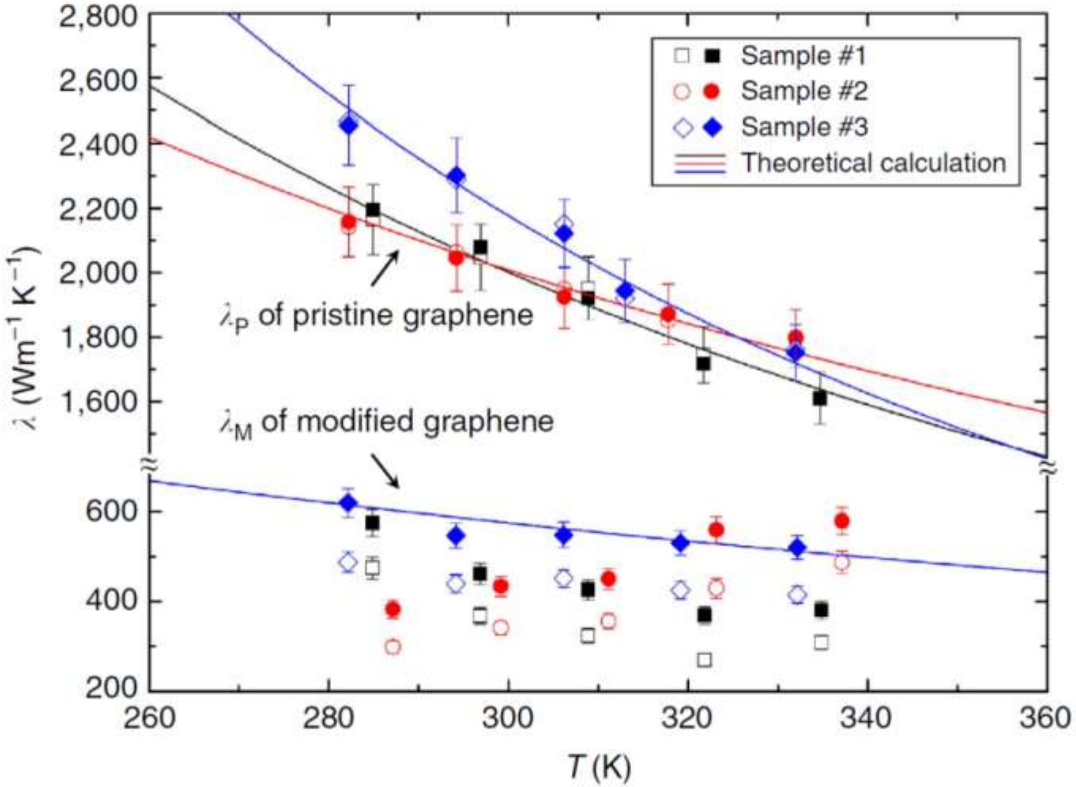
--Low D Peak shows few defects

Thermal rectification (TR) in asymmetric SLG

- **Physical mechanism:** **different temperature/space dependence of thermal conductivity of graphene. TR factor reaches 28%.**





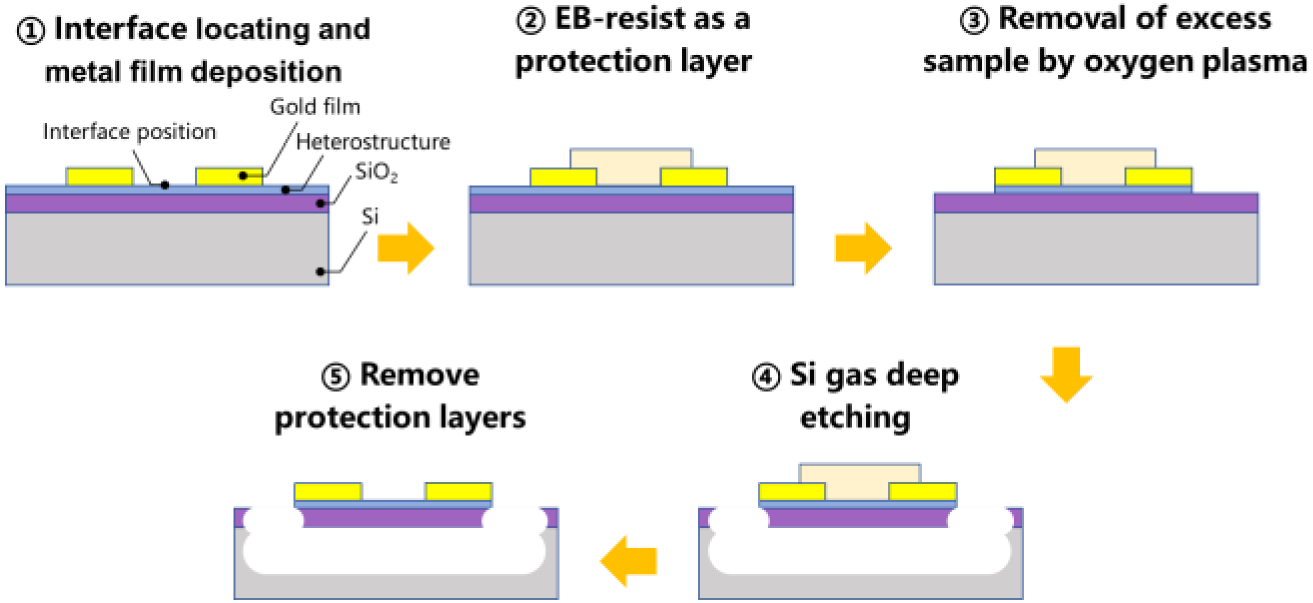


Measurement results

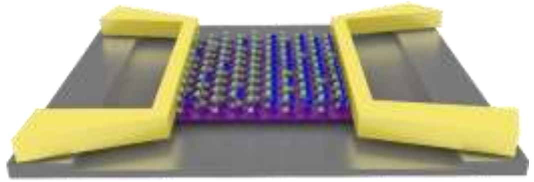
Zhang X*, et al. *Nat. Commun.*, 8, 1-8 (2017)

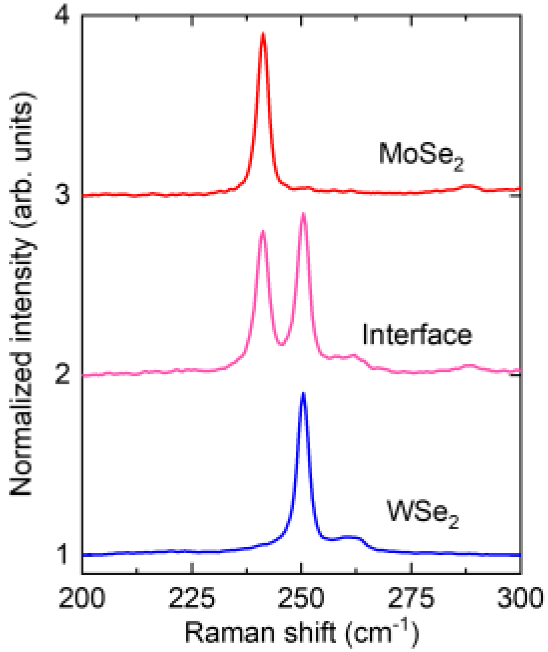
Thermal rectification in a nanodiode

■ Fabrication of a nanodiode based on a single-layer $MoSe_2$-WSe_2 heterostructure

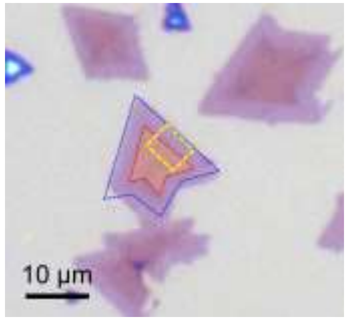


H-type nanodiode

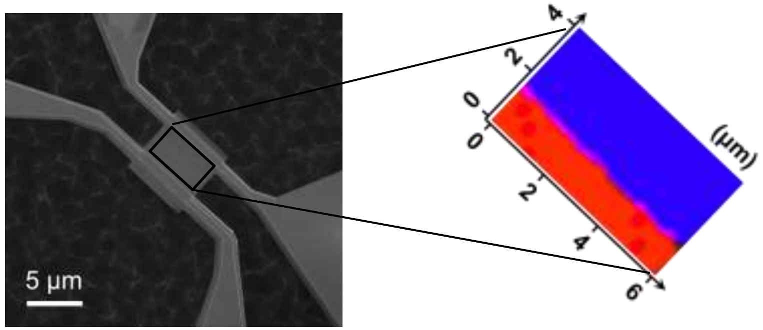




■ Characterization of H-type nanodiode



Optical image before fabrication

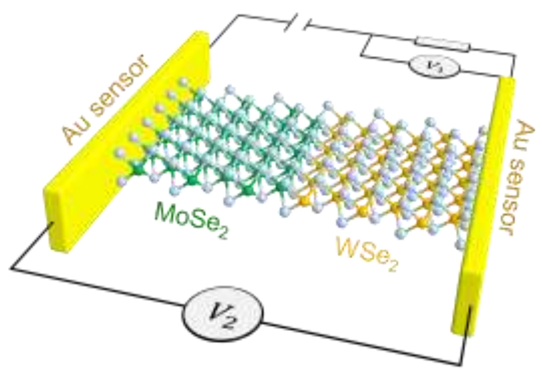


SEM image

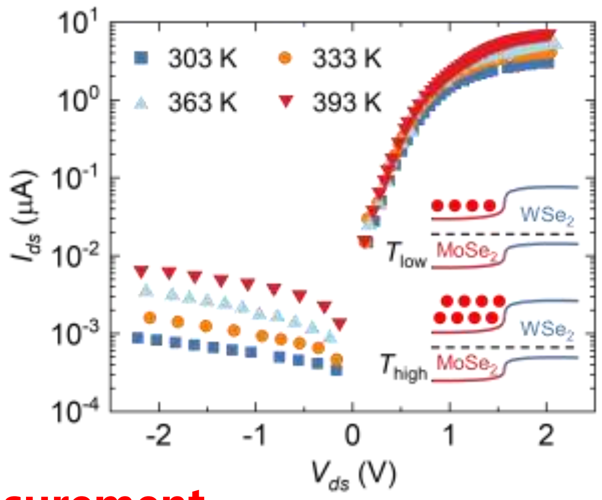
Raman mapping image

Thermal rectification in a nanodiode

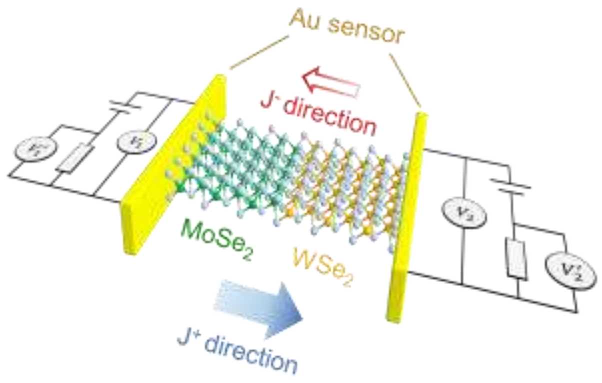
- **Electrical rectification measurement**



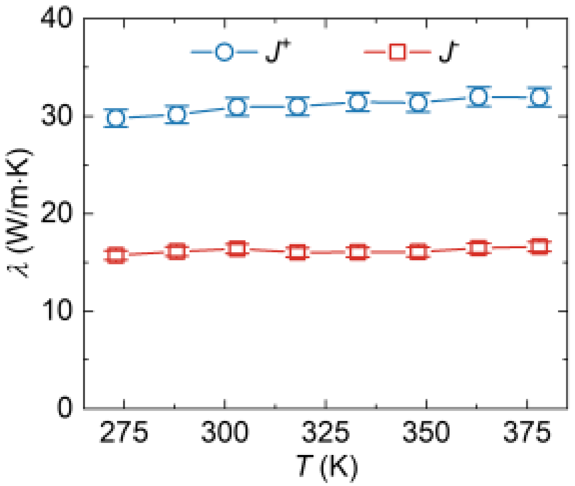
External Circuits



- **Thermal rectification measurement**



External Circuits



- **A high ON/OFF ratio of 10^4 can be achieved**
- **As the temperature increases, more carriers are excited, especially in reverse direction. For this reason, a temperature rise of 90 K leads to ~70% reduction in ON/OFF ratio**

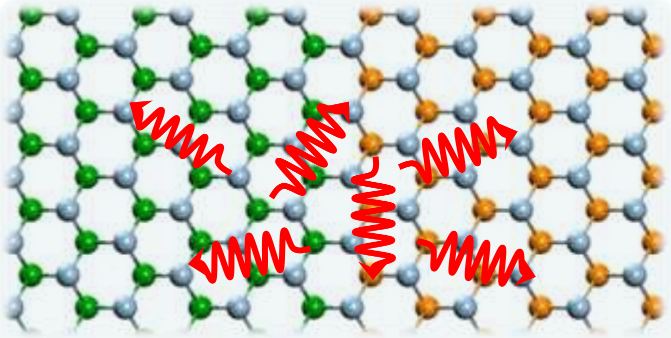
- **The thermal conductivity in the heat flow direction from $MoSe_2$ to WSe_2 is ~96% higher than that in the opposite direction**
- **It breaks the record of thermal rectification ratio for nanomaterials**

- **We realize simultaneous thermal and electrical rectification of a single nanodevice**

Thermal rectification in a nanodiode

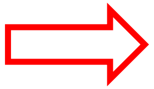
Application in heat dissipation

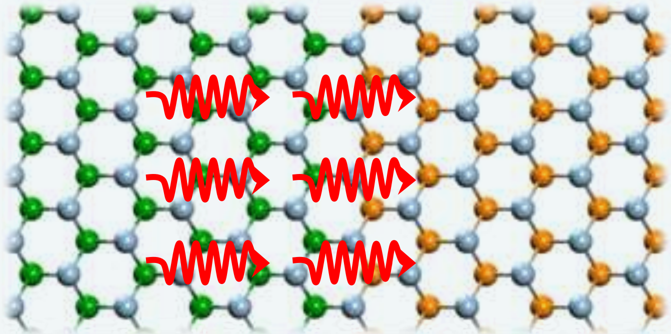
- Causes of high temperature rise in conventional diode: Heat transfer is non-directional, so the heat generated inside cannot be dissipated quickly
- Optimization strategy: unidirectional transfer of "heat" as well as "electricity "



- No thermal rectification effect
- Irregular heat transfer direction
- Low thermal conductivity

Asymmetrical design





- With thermal rectification effect
- Highly directional heat transfer
- 96% higher thermal conductivity

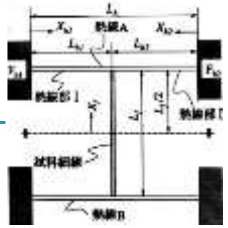
✓ Nanodiode's maximum temperature rise reduced by 20 K

✓ First time in the world to achieve comprehensive improvement of thermal and electrical performance based on a single nanodiode

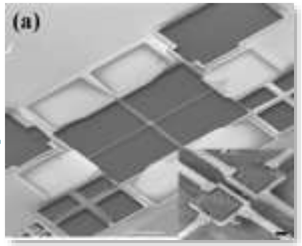
Zhang X*, et al. *Science*, 378, 169-175 (2022)

Greatness is Simplicity

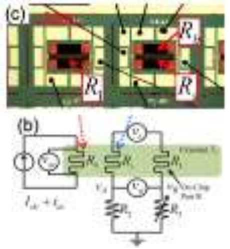
- 1998 — X. Zhang, H-type method



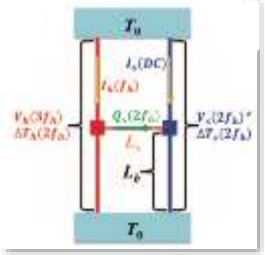
- 2001 — A. Majumdar, MSD method



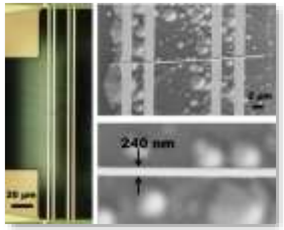
- 2012 — R. K. Chen, Eliminate fluctuations



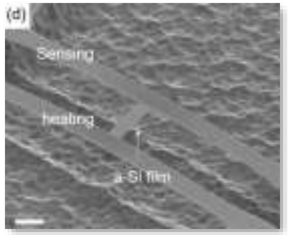
- 2013 — R. K. Chen, Eliminating current noise



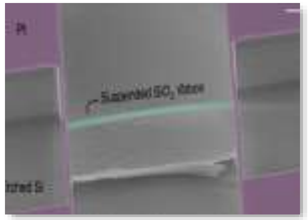
- 2012 — L. Shi, Eliminating TCR



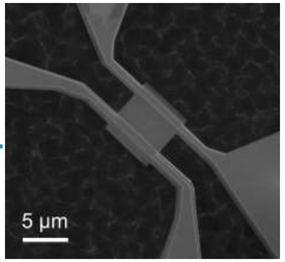
- 2017 — R. K. Chen, Si nanofilm



- 2019 — R. K. Chen, SiO_2 nanofilm



- 2022 — X. Zhang, heterojunction



➢ The **MSD method** and the **H-type method** use **similar simplified structures**, which significantly **reduce the radiation influence**.

TPMs at Nanoscale are very difficult!

Part I

Contact measurement methods for nanoscale materials

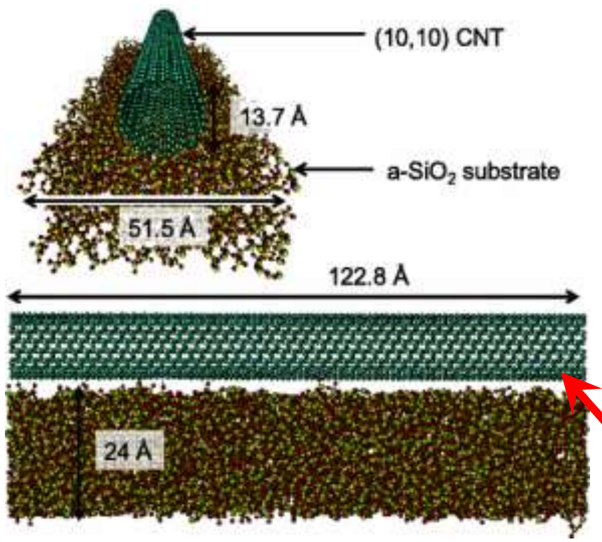
Part II

Non-contact measurement methods for nanoscale materials

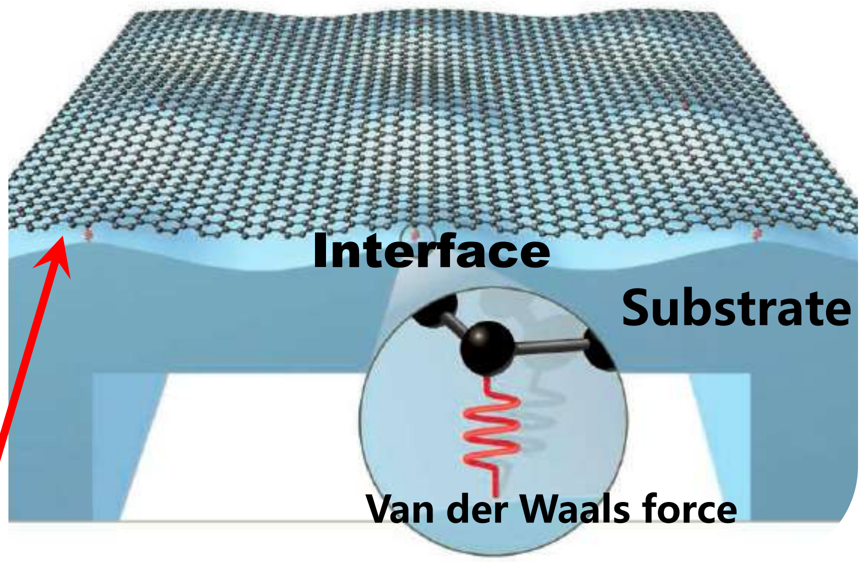
Part III

Expand applications in Multidisciplinary Research

Interfacial effect at nanoscale



Ong Z Y, Pop E, Shiomi J *Phys. Rev. B 2011*



Prasher R *Science 2010*

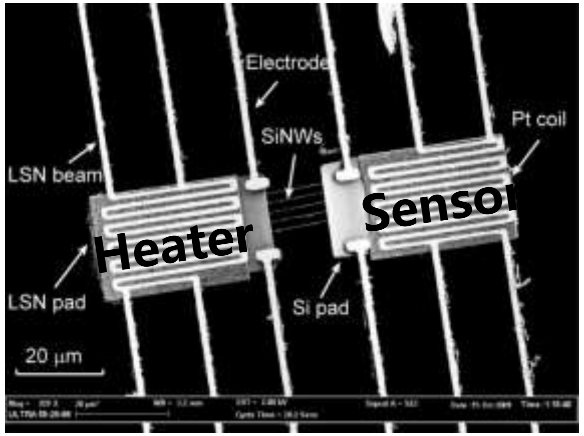
Supported nanomaterial: interfacial effects from substrate

- **MD results: the thermal conductivities of supported CNT and graphene are reduced by more than 30%~50% compared with the corresponding suspended ones.**

TPMs at Nanoscale are difficult!

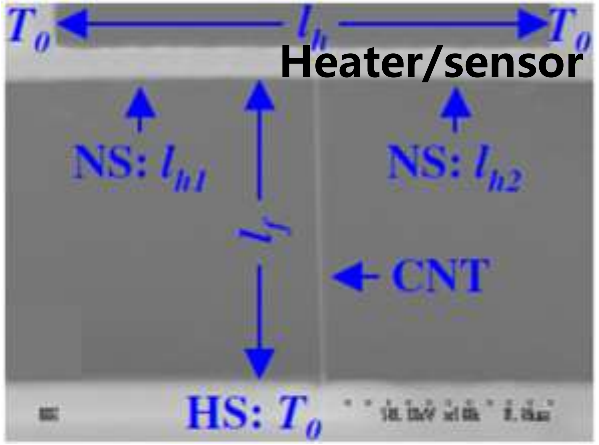
➢ For suspended nanomaterials

Suspended METS



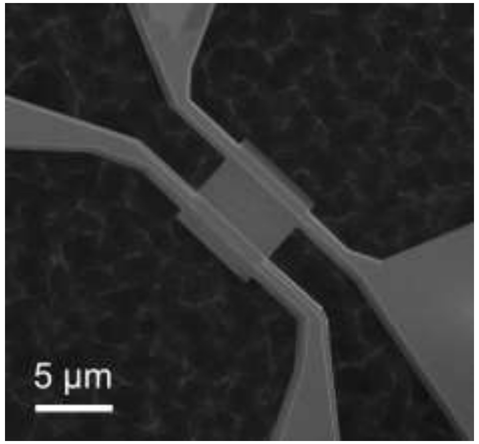
Majumdar A *et al. J. Heat Transf.* 2003
(University of California, Berkeley)

T type method



Zhang X *et al. Phys. Rev. Lett.* 2005

H type method

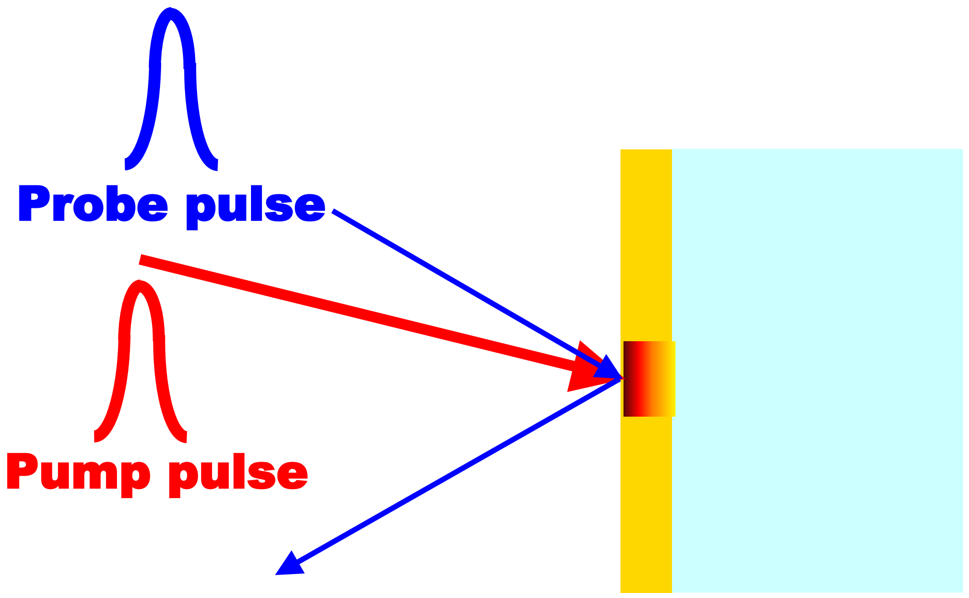


Zhang X *et al. Science.* 2022

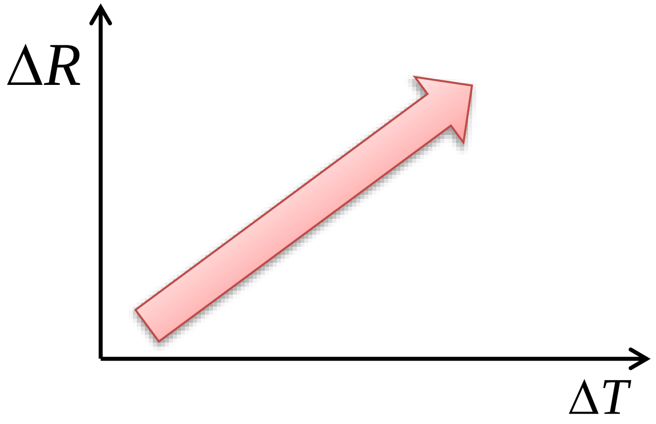
Challenge: How to in-situ measure supported nanomaterials and experimentally study the interfacial effect?

Transient thermoreflectance method

- Based on temperature-dependent reflectance.
- Pump pulse excites the film first.
- Temperature (also reflectance) changes
- Probe pulse arrives at the surface and probe the temperature at a specific time delay.

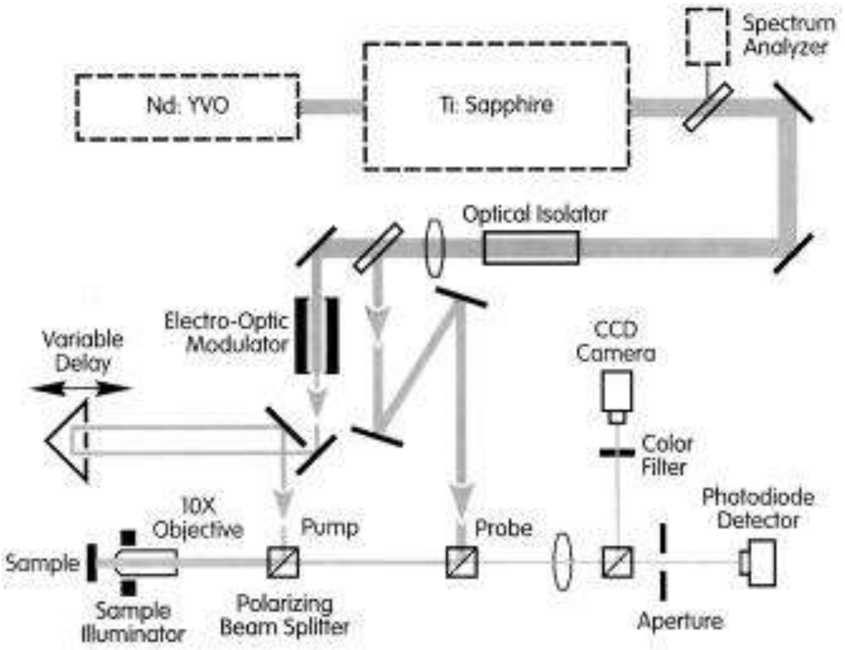


$$\Delta R = f\left(\Delta T\right)$$

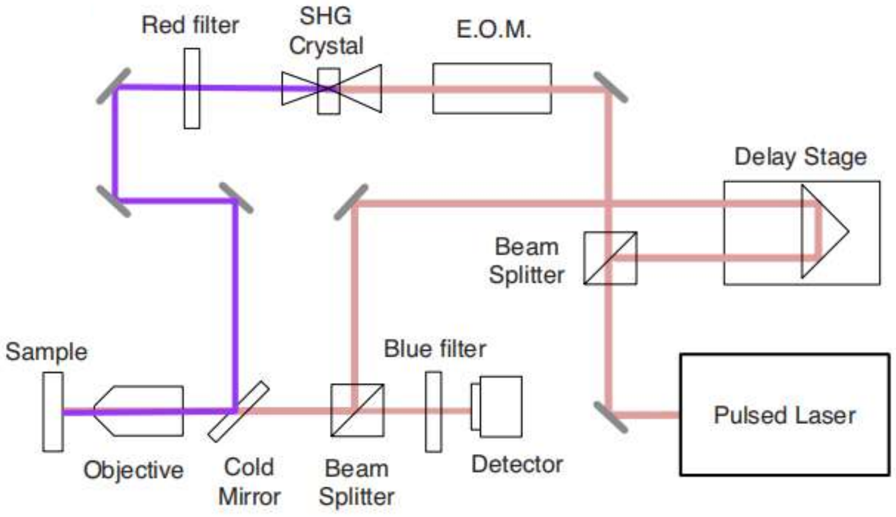


Transient thermoreflectance method

Time-Domain thermoreflectance (TDTR) ⇨ Frequency-Domain thermoreflectance (FDTR)



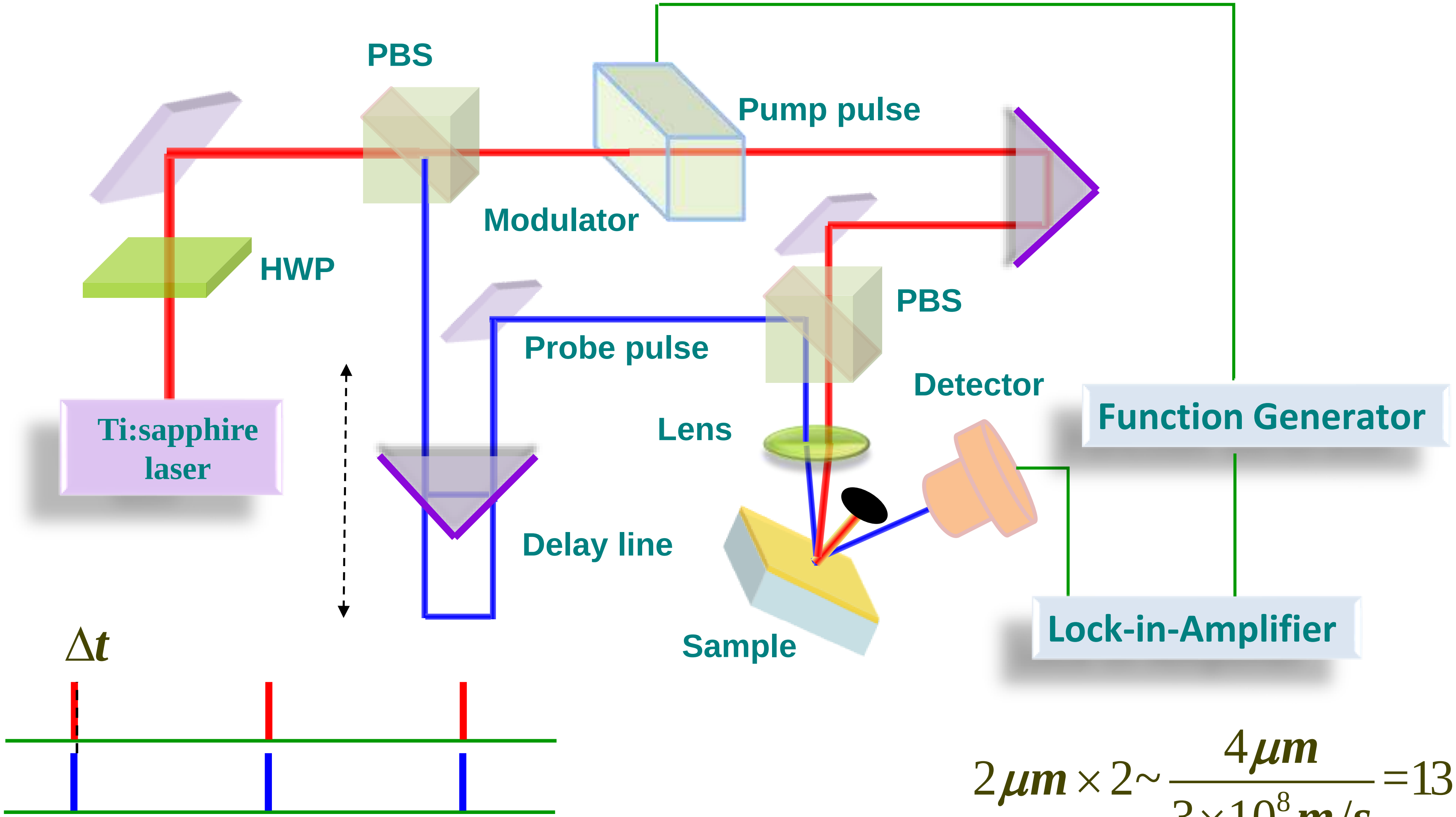
Cahill, D. G. et al.
ASME. *J. Heat Transfer*. 2002



Schmidt, A. J. et al.
Rev. Sci. Instrum. 2009

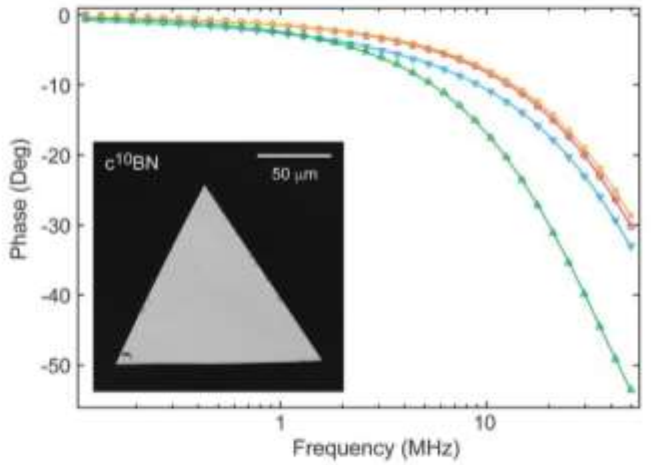
- Resolve electronic and lattice heating contributions
- TDTR can determine thermal conductivity of film in the submicron range and the thermal boundary conductance between layers
- FDTR can also determine the volumetric heat capacity simultaneously

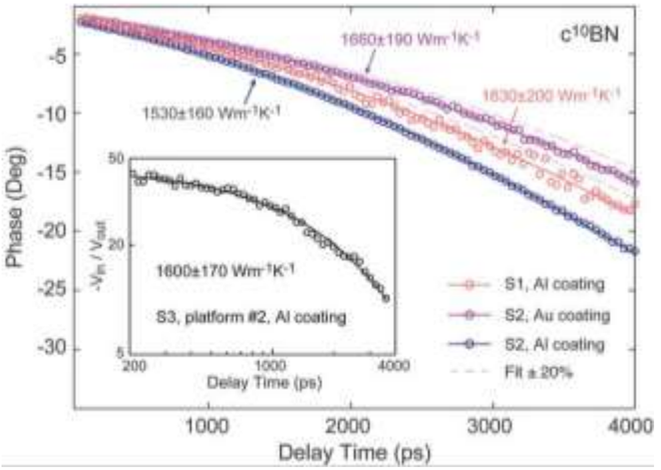
Transient thermoreflectance method



$$2\,\mu m \times 2 \sim \frac{4\,\mu m}{3\times 10^{8}\, m/s} = 13.3\, fs$$

Application of Transient thermoreflectance method

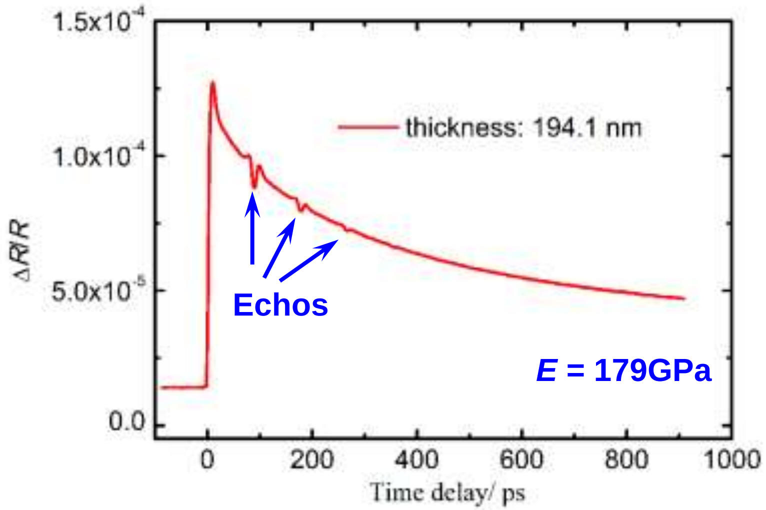




Thermal conductivity of BN

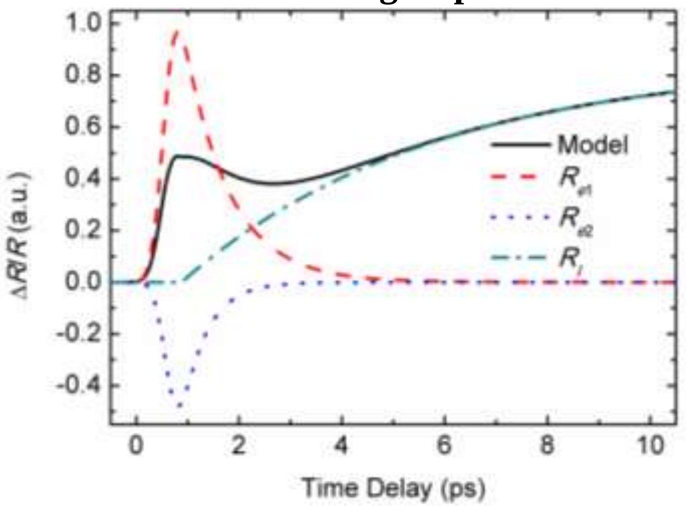
Science367,555-559(2020)

Thickness > 100 nm, atom-thick layer?



Young's modulus of $Pd_{80}Si_{20}$

Our group

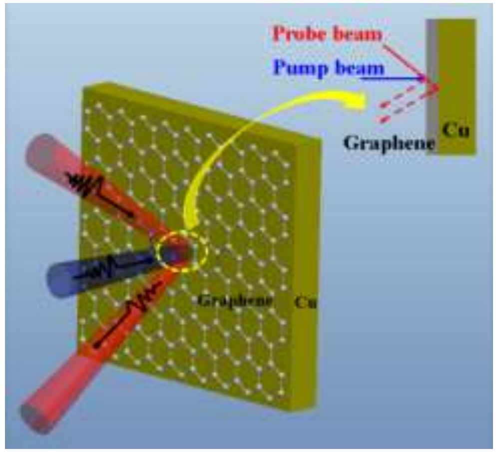


Ultrafast carrier dynamics of Bi_2Te_3

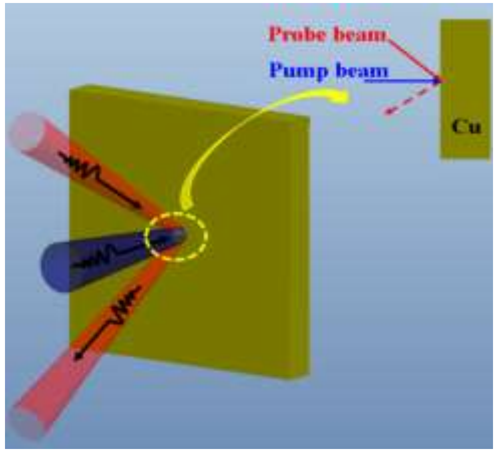
Our group

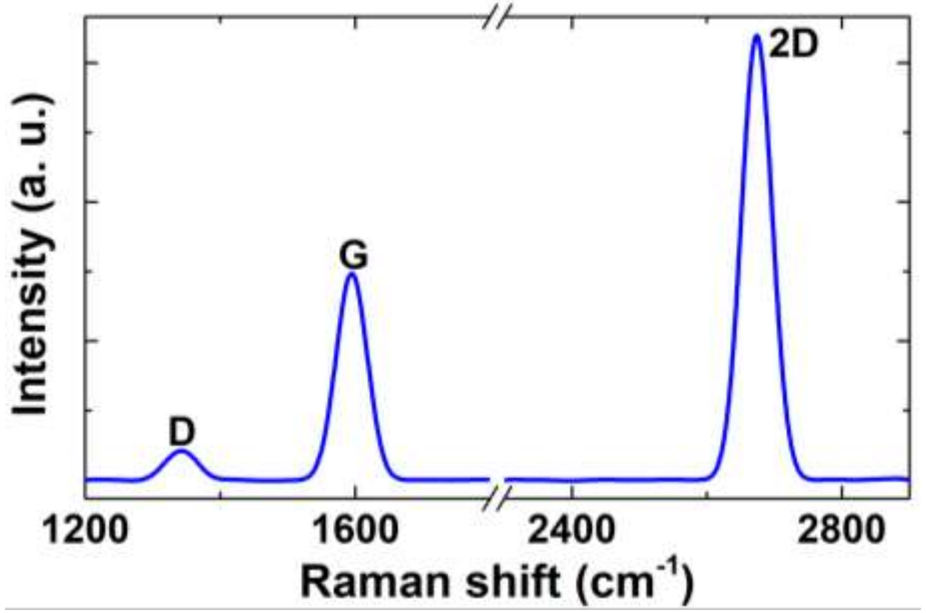
Measurement of atom-thick film

Graphene/Cu



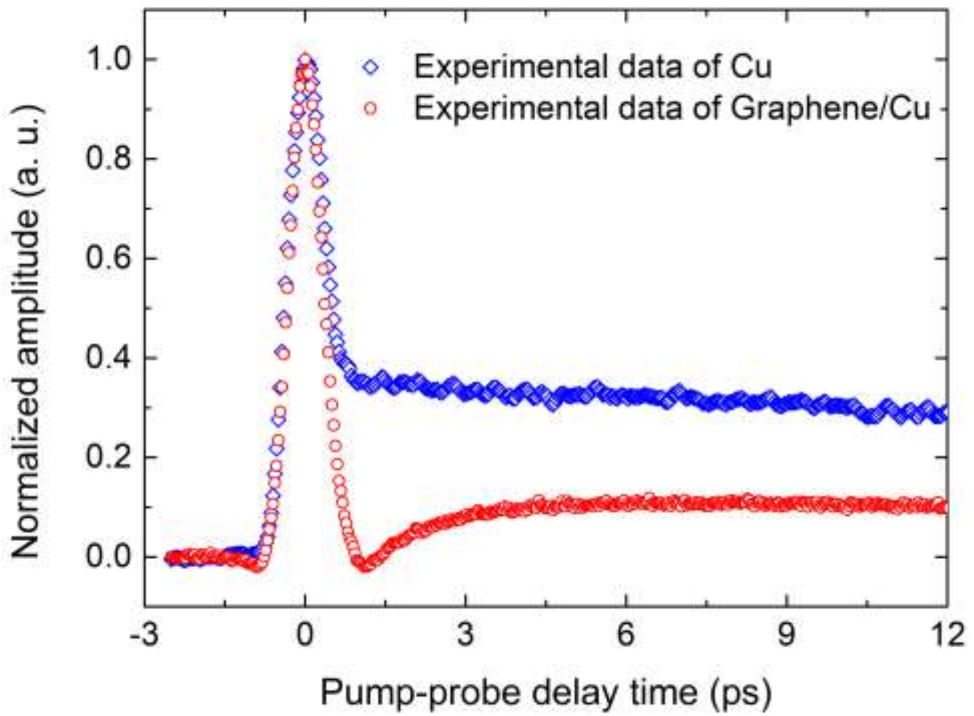
Bare Cu

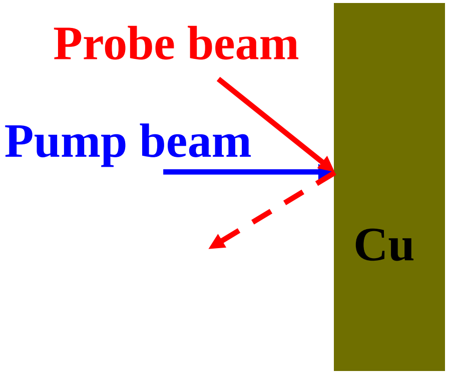


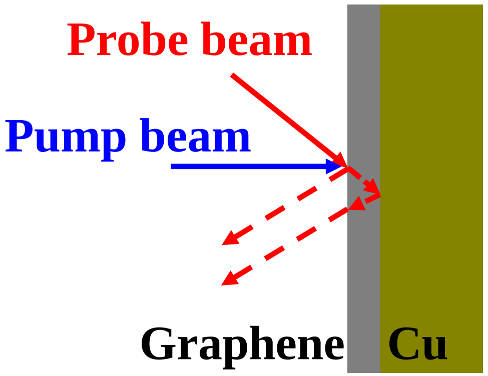


- Graphene, directly grown on Cu single crystal with high quality by CVD.
- D band, the graphene is doped.
- 2D/G~2, the grown graphene is monolayer.

Bare Cu vs. Graphene/Cu







$Re_{tot}=Re_{Cu}$

$Re_{tot}=f(Re_{Cu}, Re_{Gr}, Tr_{Gr})$

Graphene/Cu: Coupling Model

- **Graphene e-ph coupling factor:**

$$D_{measured} = 3\mathrm{eV},\quad E_{F\,measured} = 120\mathrm{meV}$$

✓ **Estimated deformation potential (D) is in the range of other studies 2-70 eV.**

✓ **Estimated from the G and 2D bands of the Raman spectrum, the Fermi level (E_F) is ~300meV, and the measured E_F is reasonable.**

- **Graphene/Cu phonon coupling factor:**

$$-\lambda_{Cul}\left.\frac{\partial T_l}{\partial x}\right|_{x=0} = G_{Gr/Cu}\left(T_{Grl} - T_{Cul}\big|_{x=0}\right),\ G_{Gr/Cu} = 50\ \mathrm{MW}\big/\left(\mathrm{m^2K}\right)$$

✓ **$G_{Gr/Cu}$ is similar with Graphene/Cu interface thermal conductance (ITC), 7~60 MW/(m^2K)**

Int J Heat Mass Tran 197 (2022) 123322

Nanoscale measurement methods

➢ For non- contact methods

TDTR

1. Need a metal film transducer (reflectivity ∝ temperature)
2. Transducer thickness > 10 nm
3. Extract thermophysical properties from <u>the single temperature curve</u> of the transducer

Raman

1. Simultaneously detect the temperatures of each layer from their *T*-dependent Raman spectra
2. Detect the temperature of the atomic thick material
3. Promising to extract properties from multiple temperature curves of each layer

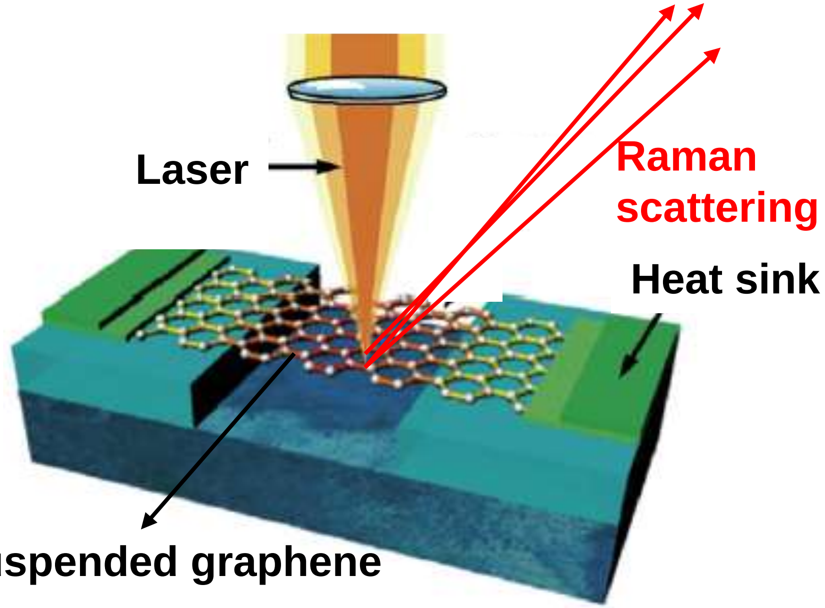
Raman – a promising approach to measure nanomaterials

- ➢ A high temporal/spatial resolution Raman measurement method
- ➢ Comprehensive sensitivity analysis to reach the most sensitive region

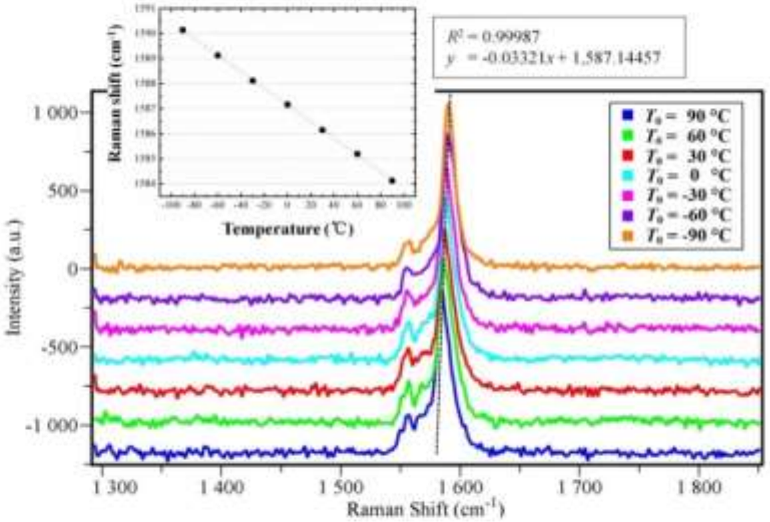
Raman-based thermometry

Principle:

1. Laser heats the sample and excites Raman spectra
2. Raman band shifts change linearly with temperature



Balandin A et al., Nano Lett. 2008



Temperature dependent Raman spectra of SWCNT

Zhang X et al. Nanosc. Microsc. Therm. 2013*

Raman-based thermometry has been used to measure the thermal conductivity of suspended graphene, MoS_2, CNT, Si/Ge nanowires

Development of Raman-based measurements

➢ Steady-state Raman method (Balandin 2008)

✓ Determine thermal conductivity of nanomaterial

χ Laser absorptivity affects the measurement accuracy

laser absorptivity is hard to be determined at the nanoscale

$$\boxed{\lambda = -\frac{\eta q}{dT/dx}}$$

$$\Downarrow$$

$$\boxed{\alpha = \frac{\lambda}{\rho c_p}}$$

➢ Transient Raman method

(X. Zhang 2014)
(X. Wang 2015)

➢ Determined thermal diffusivity of nanomaterial

✓ Eliminate the influence of laser absorptivity by normalization method

χ Temporal resolution needs to be improved

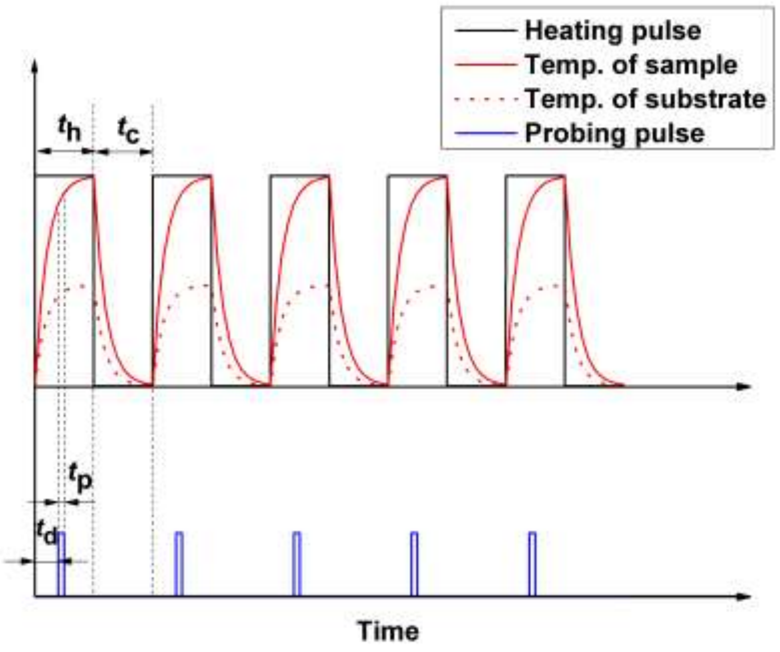
Temporal resolution is limited by the rising edge of the electro-optical modulator (EOM) which are still not satisfactory and will affect the measurement accuracy.

⇩

Dual-wavelength Flash Raman (DFR) principle

Principle of DFR

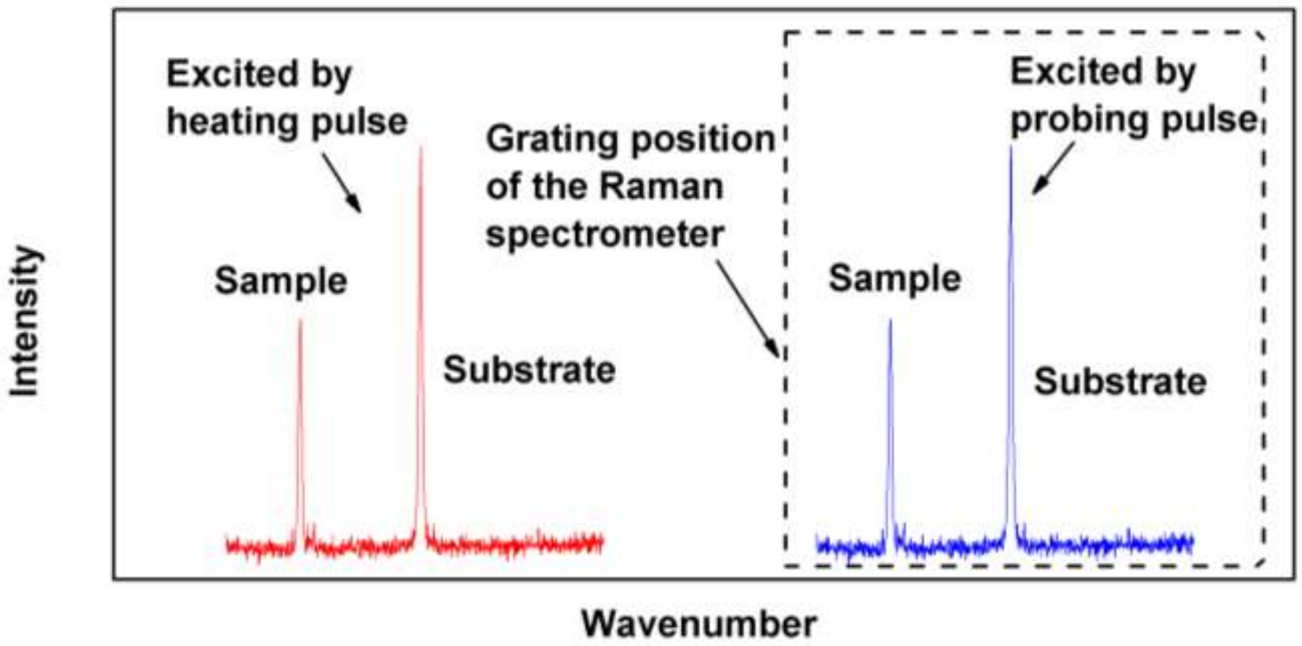
➢ Dual Flash – Heating pulse & Probing pulse



- **Heating pulse: heat the sample**
- **Probing pulse: heating effect can be eliminated, different wavelength from heating pulse (only detect the Raman spectra excited by the probing pulse)**
- **The deviation t_d : changed by the signal generator**

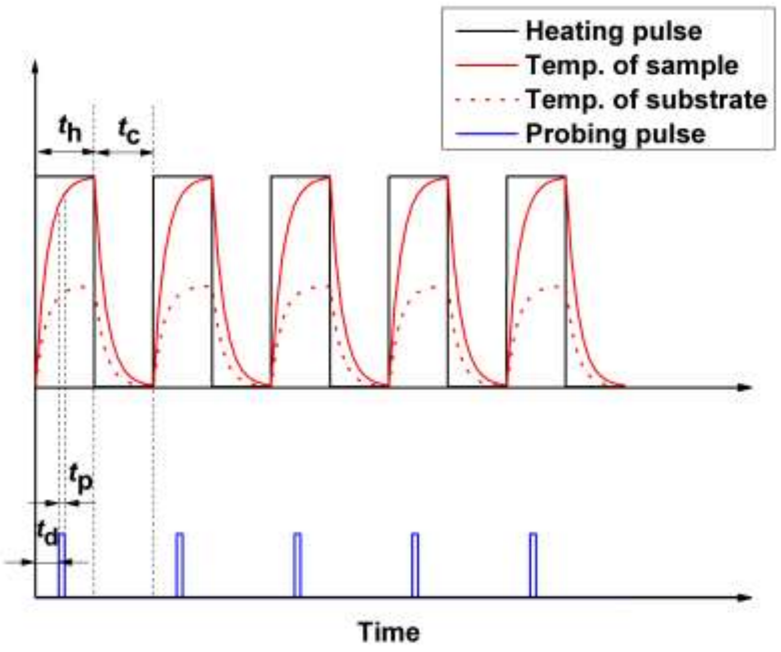
Principle of DFR

➢ Dual-wavelength laser



- Different wavelength to **distinguish** the Raman spectra excited by **the heating laser** and **the probing laser**

Principle of DFR



- **Heating pulse: heat the sample**
- **Probing pulse: heating effect can be eliminated, different wavelength from heating pulse (only detect the Raman spectra excited by the probing pulse)**
- **The deviation t_d : changed by the signal generator**

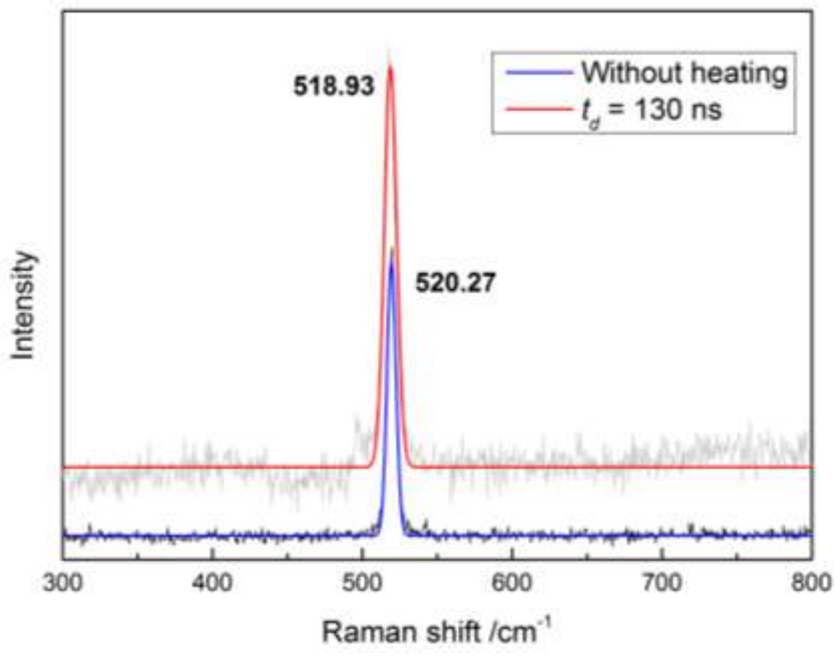
➢ **Significantly enhance the temporal resolution (10ns to ~0.1ns)**

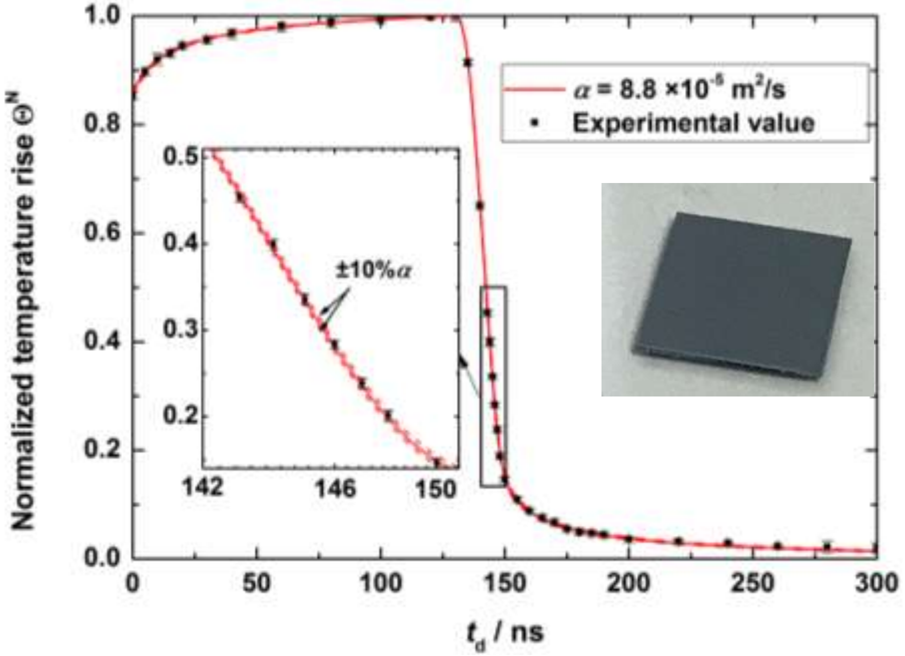
➢ **Eliminate the influence of the laser absorptivity of the sample directly in cooling proceeding**

➢ **In heating proceeding, the influence of the laser absorptivity can be eliminated by normalization analysis**

Experimental verification (Silicon)

- t_h= 150 ns, t_p=20 ns, highest temperature rise = 67 K.





- **The difference** between the measured value and the average literature data of bulk silicon is **within 3%**
- The **reliability and accuracy** of the measurement method and system **have been verified.**

Zhang X*, et al. Journal of Thermal Science 2019, 28(2): 159-168

How to get more spatial information?

➢ Advantages

- ✓ High temporal resolution
- ✓ Eliminate the influence of laser absorptivity
- ✓ Measure the thermal diffusivity of suspended nanomaterials with high sensitivity
- ✓ Can be used to measure the thermal diffusivity of supported nanomaterials

➢ Limitations

- X For supported superfine nanofibers with high thermal diffusivity, measurement sensitivity is still unsatisfactory
- X Cannot measure anisotropy materials

⇩ To improve sensitivity & to extend application range

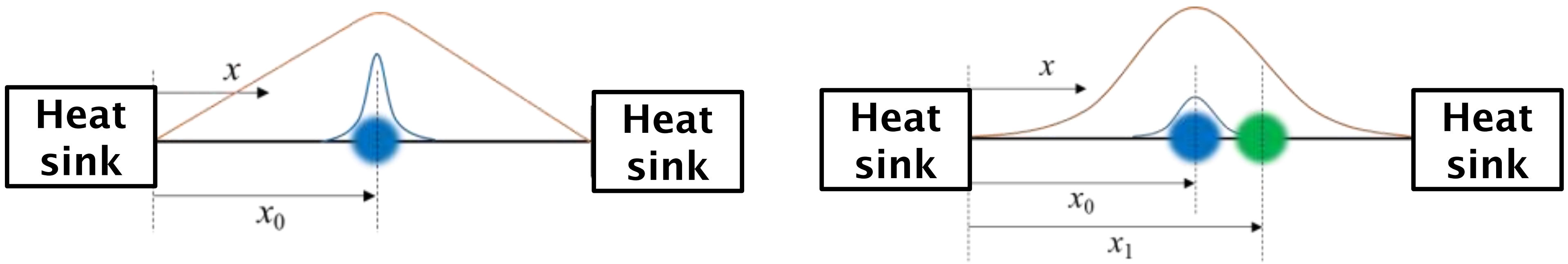
DFR mapping method

DFR mapping method

- Measurement sensitivity of coaxial DFR method is still unsatisfactory for supported superfine nanofiber with high thermal diffusivity.

- **How to further improve the measurement sensitivity ?**

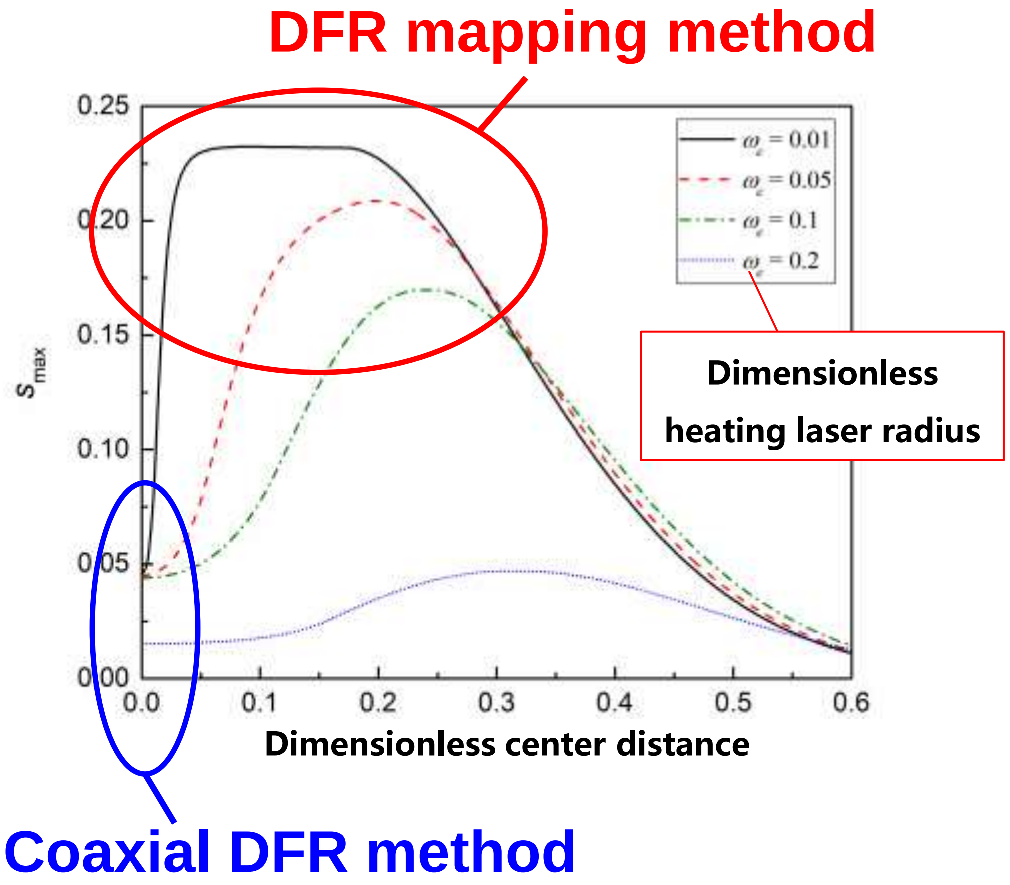
DFR mapping method

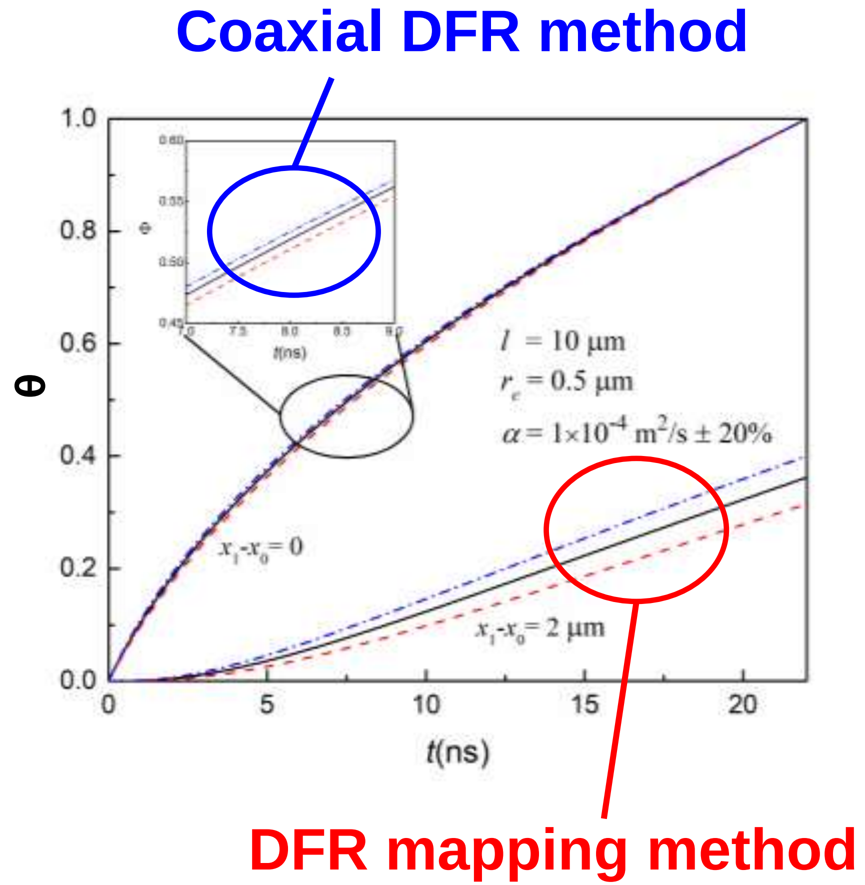


- **Fixed heating laser spot**
- **Change the position of probing laser spot**
- **Determine the temperature variation curves at different position**

Coaxial VS. Mapping method

Sensitivity of the DFR mapping method can be more than 4 times of it of coaxial DFR method for the thermal diffusivity measurement





Zhang X* et al. Int J Heat Mass Tran, 2019, 143: 118460

Challenge of Raman thermometer

➢ For the Raman-based method

- Temperature measurement sensitivity is limited by the temperature versus Raman band shift relationship of the sample
- For nanomaterial, low sensitivity of temperature measurement results in large measurement uncertainty of the thermophysical properties
- Measurement uncertainty of the normalization characteristic temperature will increase the measurement uncertainty of the measured data

⇩ Reduce measurement uncertainty

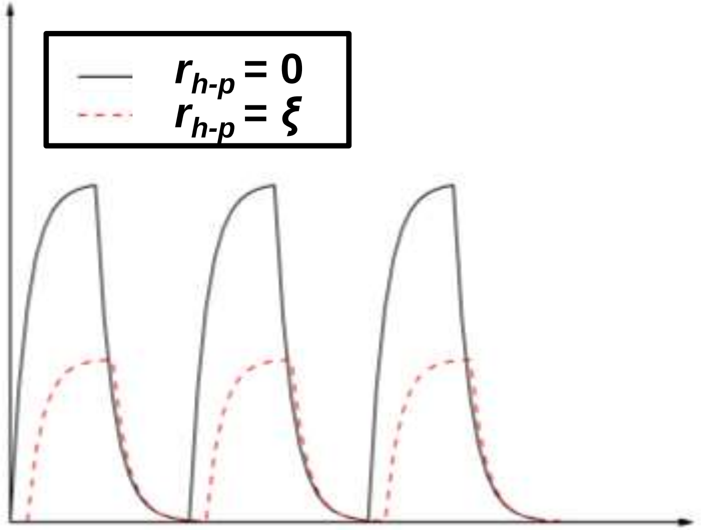
Phase method

Phase Method

- Measurement uncertainty of the normalization characteristic temperature will increase the measurement uncertainty of the measured data

Temperature Phase Definition

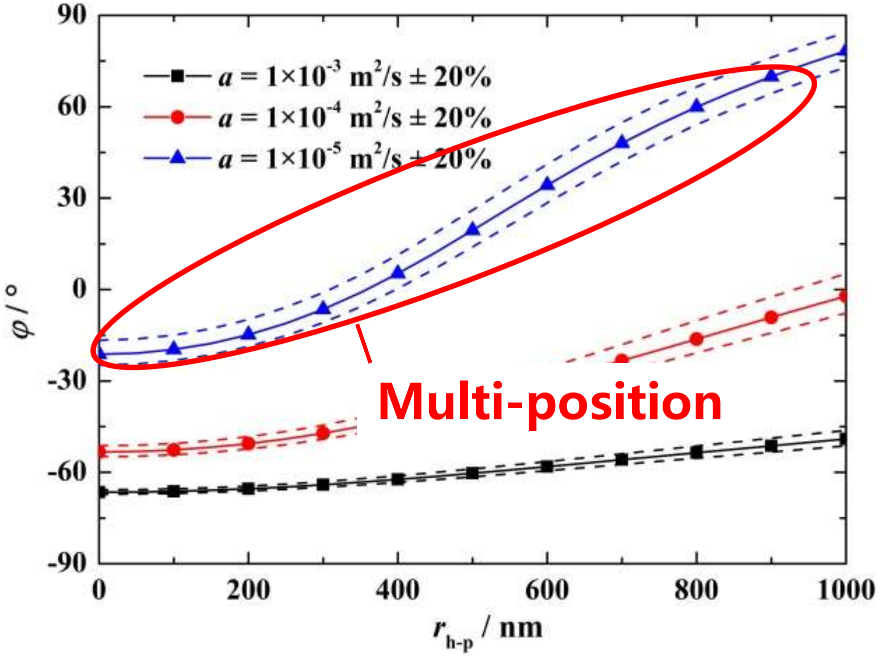
$$\varphi = \arctan\left[\frac{\int_0^{2t_h} T_i \sin(\omega t_i)dt}{\int_0^{2t_h} T_i \cos(\omega t_i)dt}\right]$$

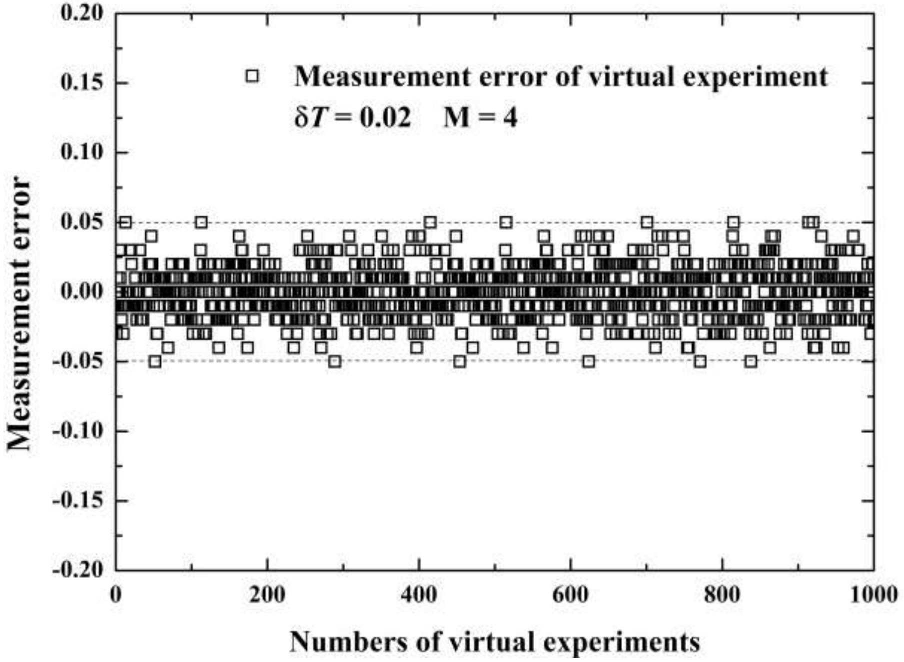


- A temperature phase is proposed to describe the shape of the temperature variation curves at different position
- Thermal diffusivity can be characterized by the temperature phase

Multi-position phase method

➢ Uncertainty analysis with multi-position phase



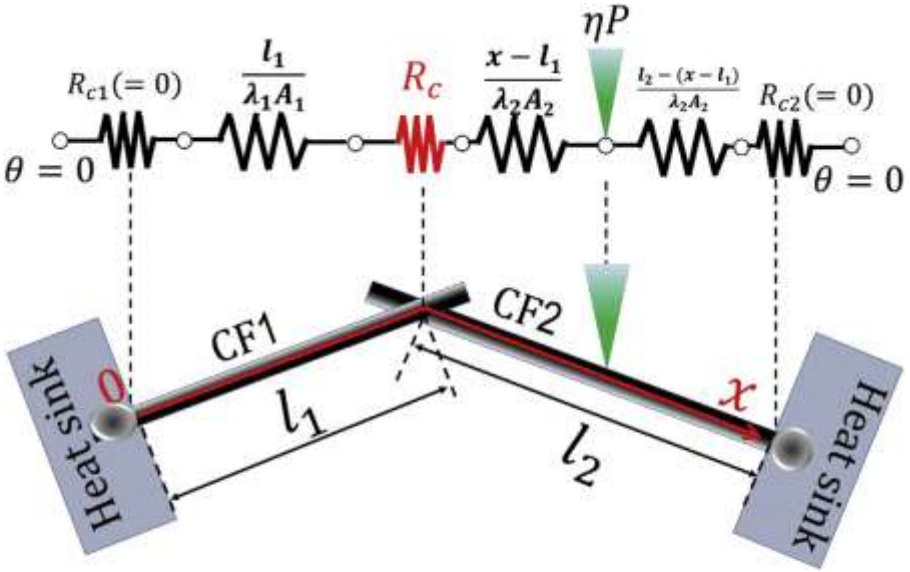


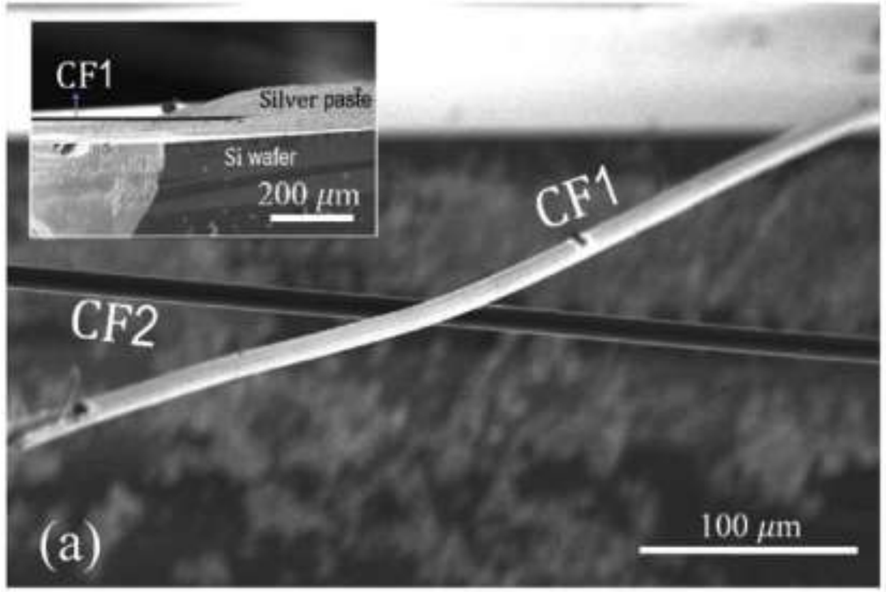
- With multi-position phase analysis, when the uncertainty of the temperature measurement is ±2% and each temperature measurement repeats 4 times, the uncertainty of the measured thermal diffusivity can reach ±5%

Zhang X* et al. Int J Heat Mass Tran, 2019, 143: 118460

0-D Application

1. Point thermal contact resistance of carbon fiber (CF)



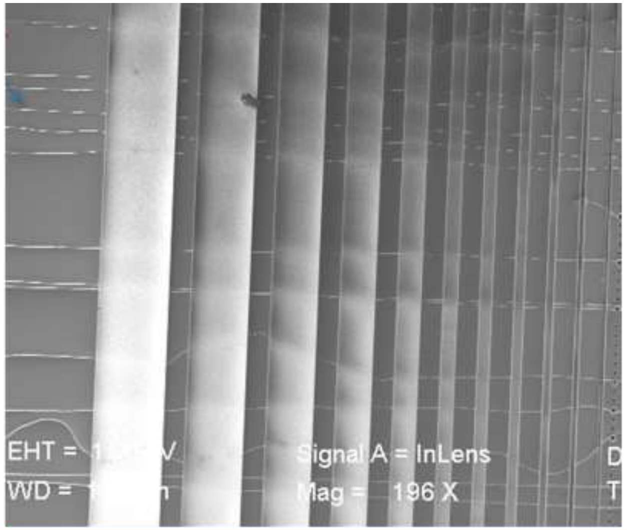


- Total thermal resistance as a function of *x*, and the point thermal contact resistance can be extracted as (2.98 ± 0.51) $\times 10^5$ K/W
- The first time to characterize 0-D TCR between carbon fibers by a non-contact measurement method

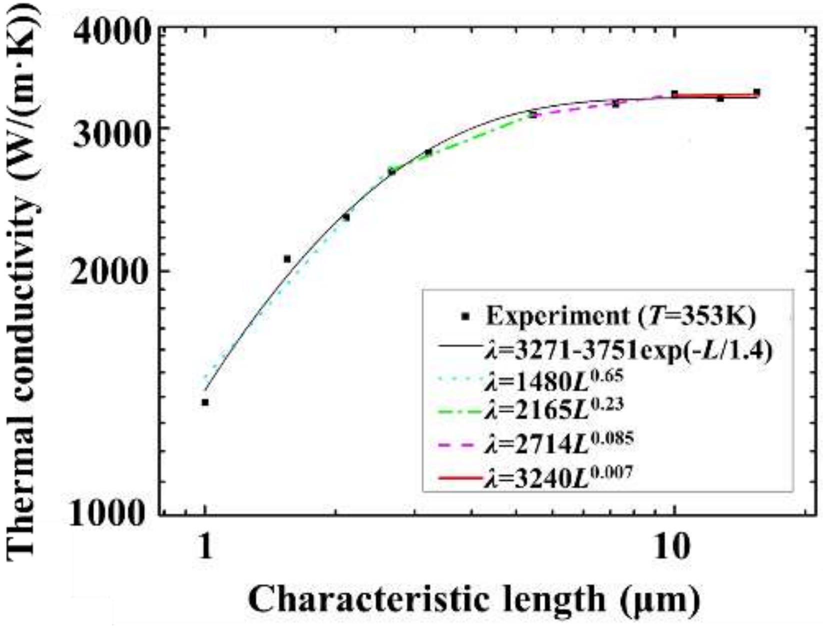
1-D Applications

2. length dependent thermal conductivity of SWCNT

- Different width trenches



w=1, 2, 3, 4, 5, 6, 10, 15, 20, 25, 30 μm

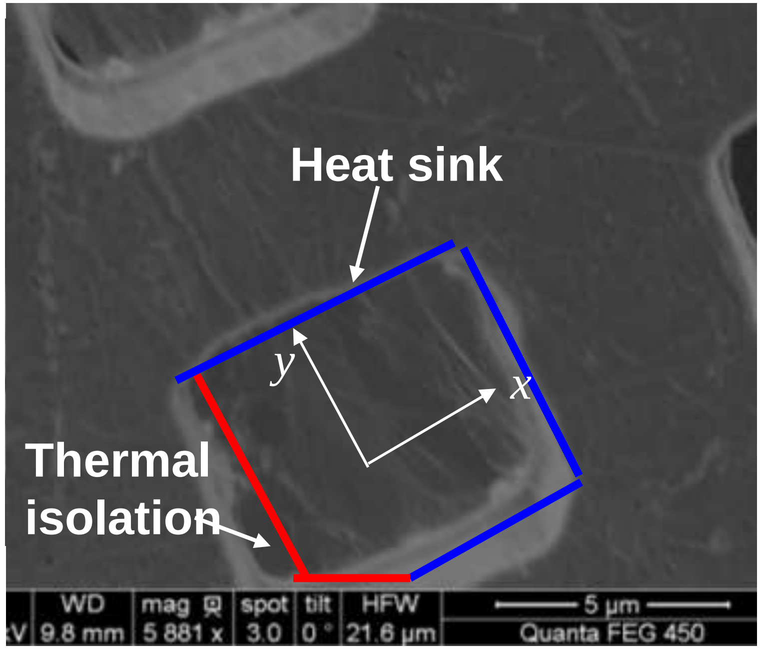


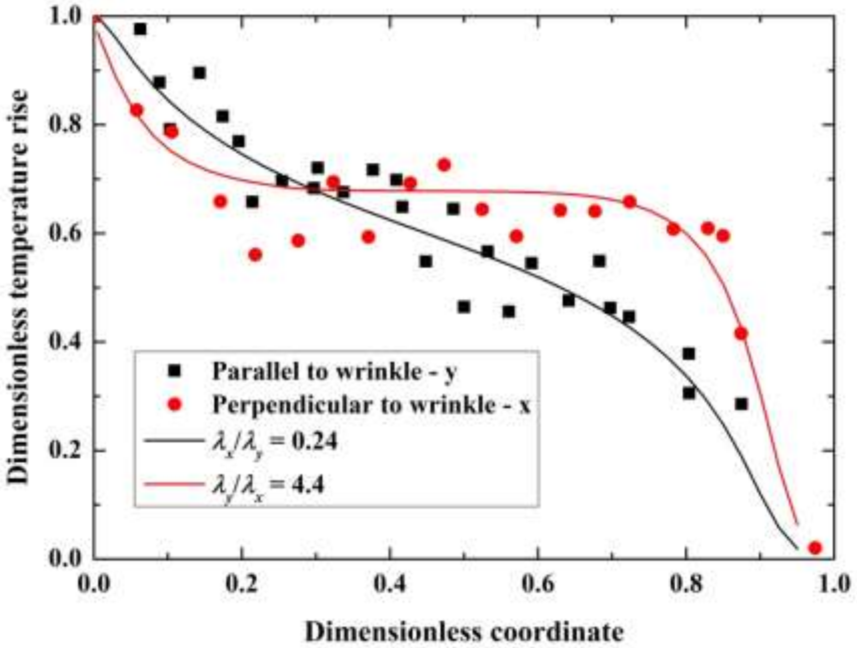
- SWCNT radius is 1.28 nm
- Thermal conductivity first increases with increasing characteristic length and then saturates to a finite constant value at a characteristic length of ~10 μm

2-D Applications

3. Wrinkle influence on thermal transport of graphene

➢ **Anisotropy analysis**





- **For wrinkled graphene, the thermal conductivity parallel to wrinkle is 4.4 times of the thermal conductivity perpendicular to wrinkle**

DFR Principle Summary

Steady-state Raman

Transient Raman

Coaxial DFR Raman

DFR mapping Raman

Measurement methods

Data processing methods

Normalization method

Phase method

Heat conduction models

- Suspended 1D, 2D
- Supported 1D, 2D
- Anisotropy material

TPMs at Nanoscale are very difficult!

Part I

Contact measurement methods for nanoscale materials

Part II

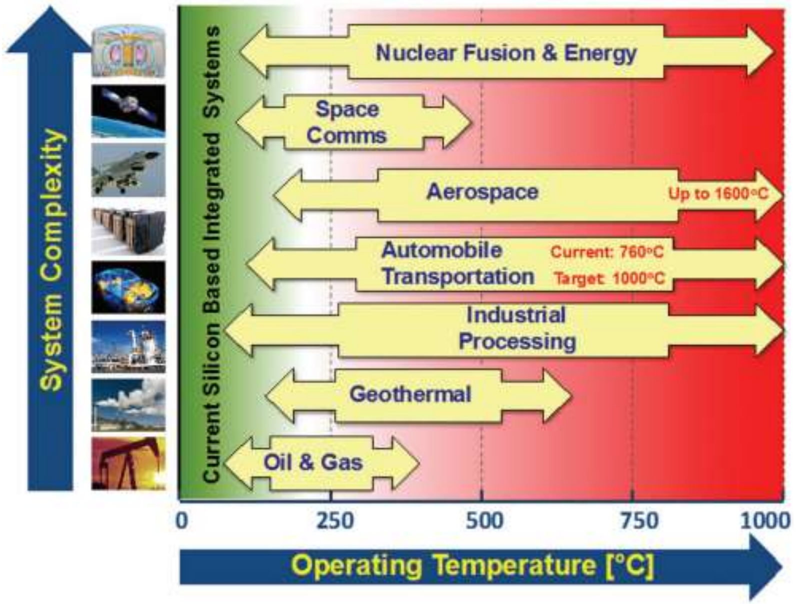
Non-contact measurement methods for nanoscale materials

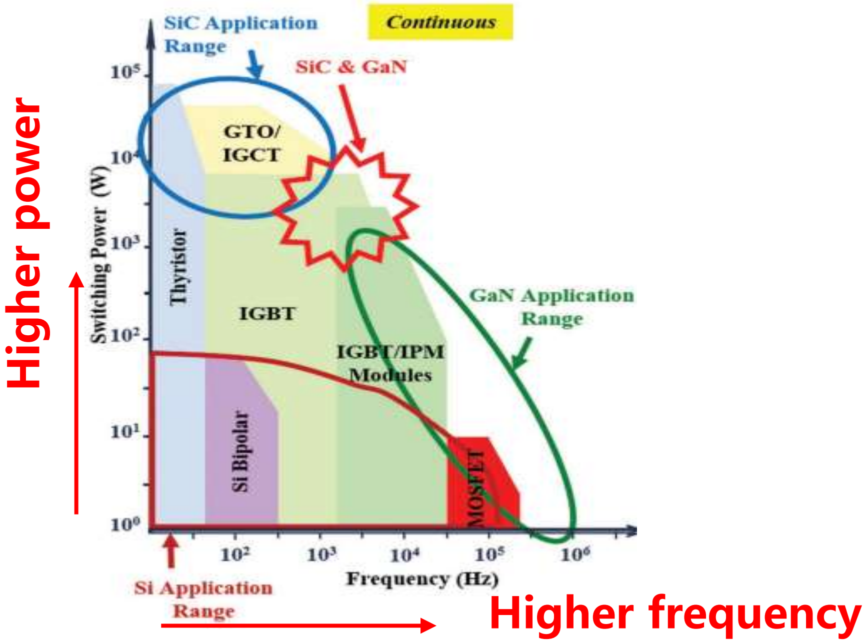
Part III

Expand applications in Multidisciplinary Research

Background

- **Power devices** are core components of power electronic equipments
- **To improve the energy conversion efficiency, power devices need to develop towards higher power and higher operating frequency**

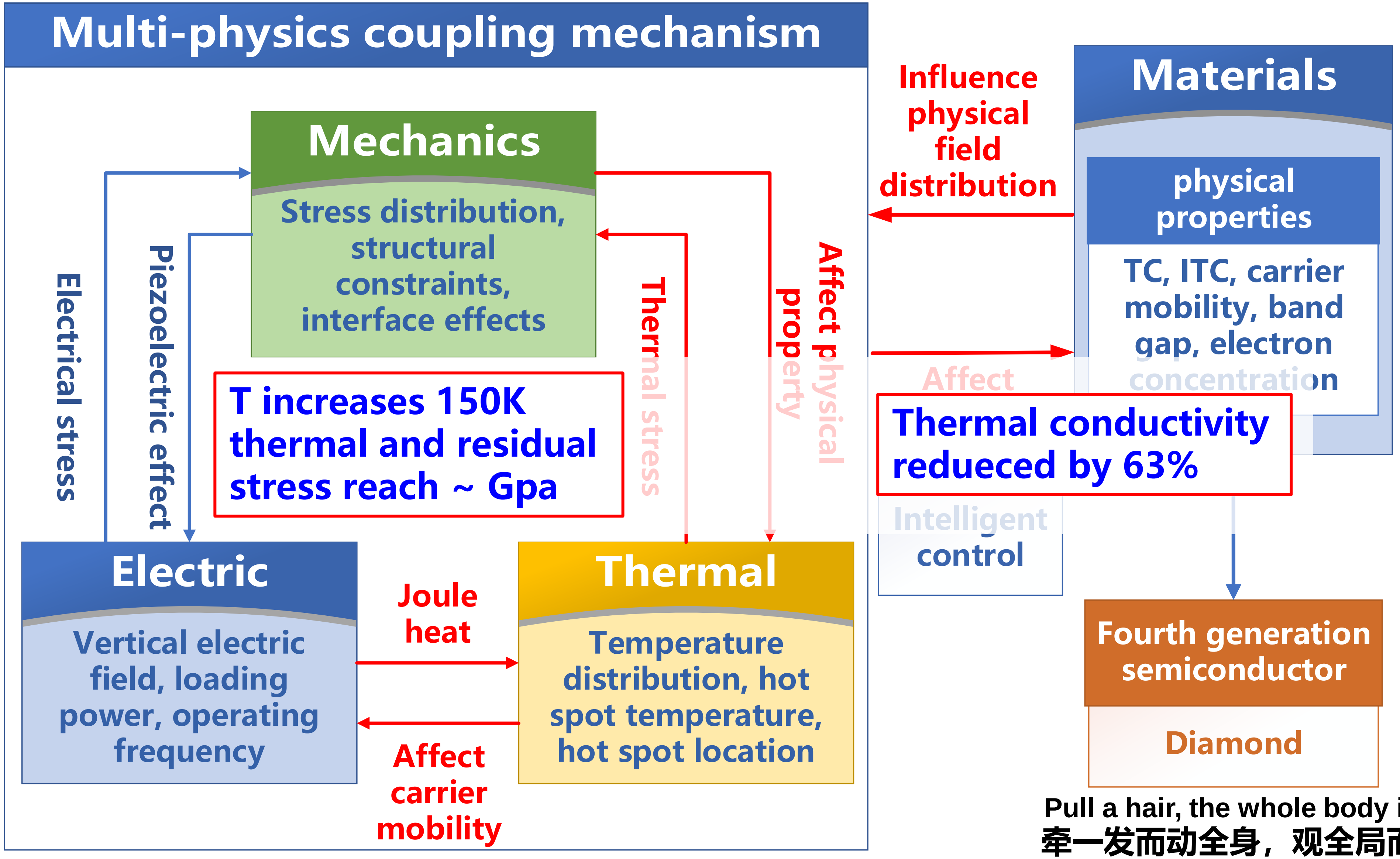




- **Cooling problem has become a critical bottleneck**

> **Developing novel semiconductor materials and optimizing device design are essential approaches to solve the cooling problem**

Multidisciplinary integrated optimization

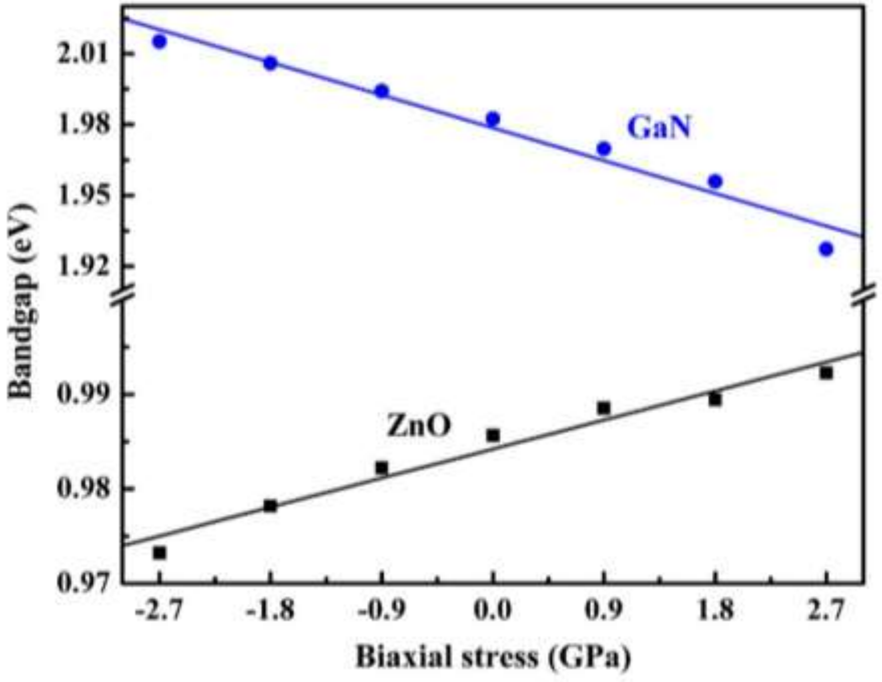


Pull a hair, the whole body is affected
牵一发而动全身，观全局而治要害

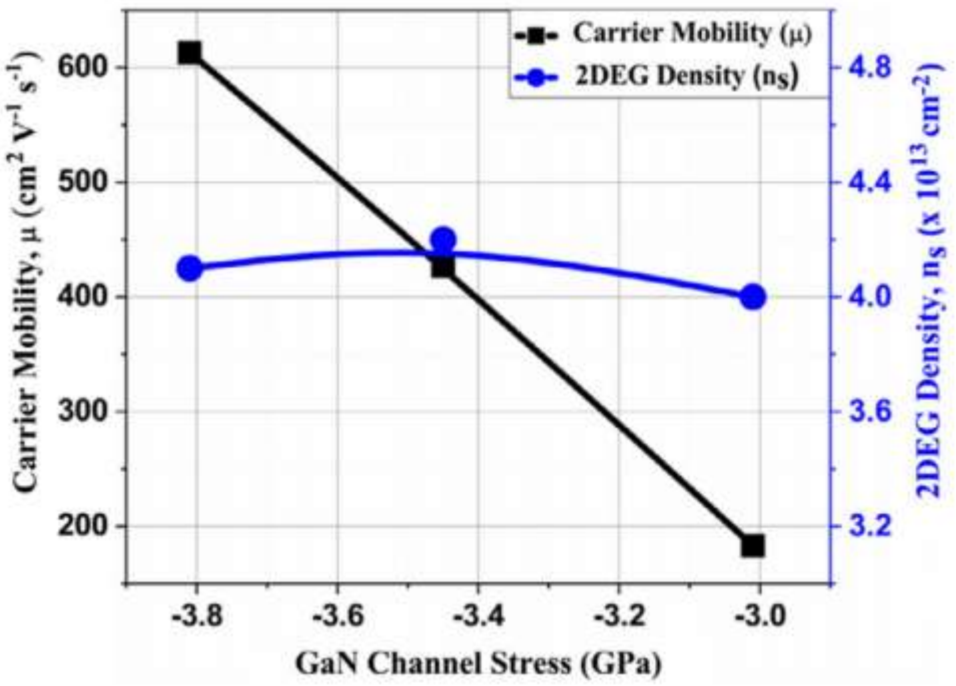
Only when we grasp the inherent rules among them, can we do the MOD for a power device.

Stress also affects electrical properties

- In addition to thermal properties, stress can also lead to significant deterioration of the electrical properties, which accelerates device failure



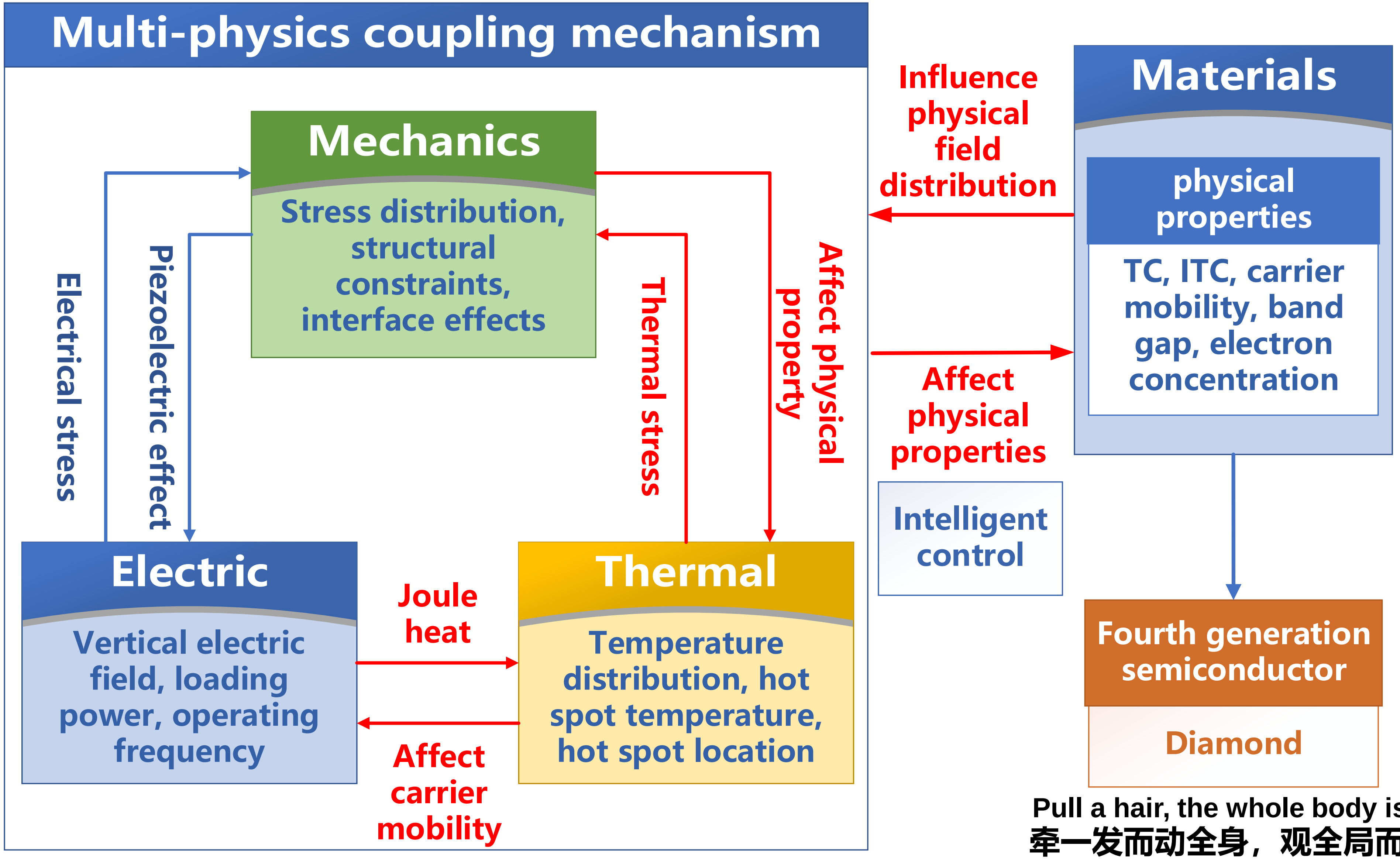
Li Y F et al. Journal of Applied Physics, 2008, 104(8):383.



Patwal S et al. Physica status solidi, 2020, 217(7):1900818.1-1900818.7.

- When the in-plane tensile stress increases by 1GPa, the bandgap decreases by 0.015eV.
- The loaded compressive stress decreases from 3.8 to 3.0GPa, and the carrier mobility of GaN heterostructure decreases from 613 to 183 $cm^2V^{-1}s^{-1}$.

Multidisciplinary integrated optimization



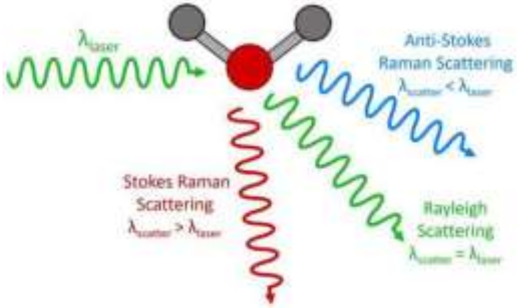
Pull a hair, the whole body is affected

牵一发而动全身，观全局而治要害

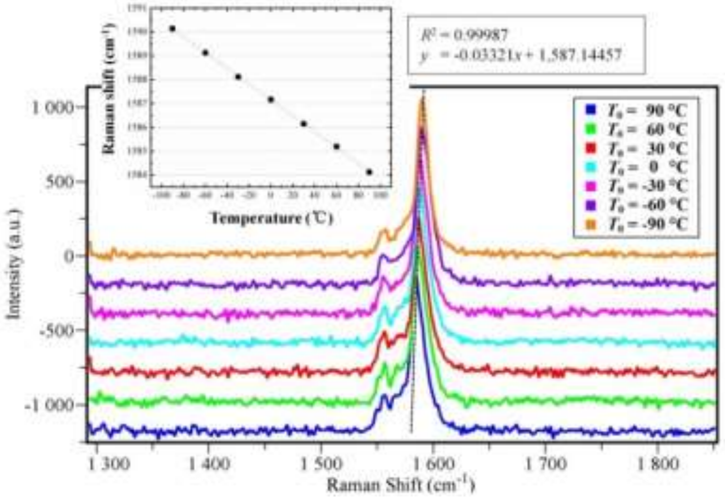
Only when we grasp the inherent rules among them, can we do the MOD for a power device.

Integrated measurement
—— based on Raman spectroscopy method

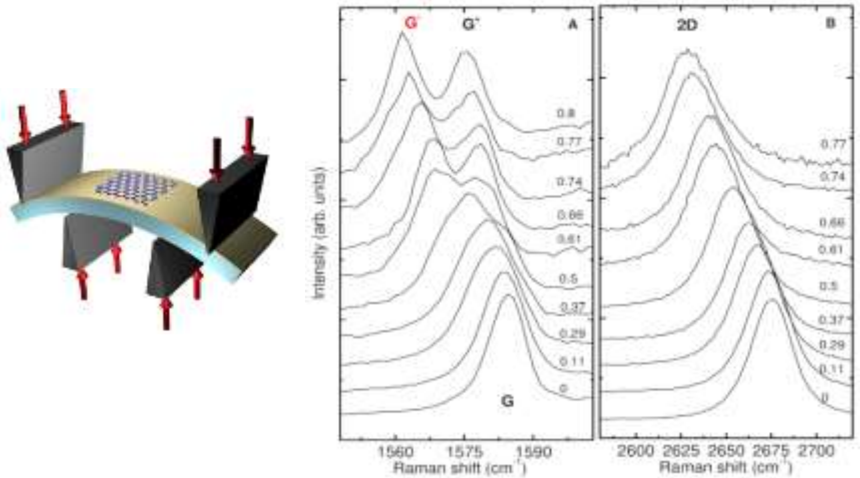
- **Raman spectroscopy is a fingerprint with the advantages of non-contact, penetrability and high spatial resolution (~1μm)**
- **Based on accurate Raman shift coefficient, Raman spectroscopy can effectively realize the measurement of temperature, stress or even electric field separately**



Inelastic Raman scattering



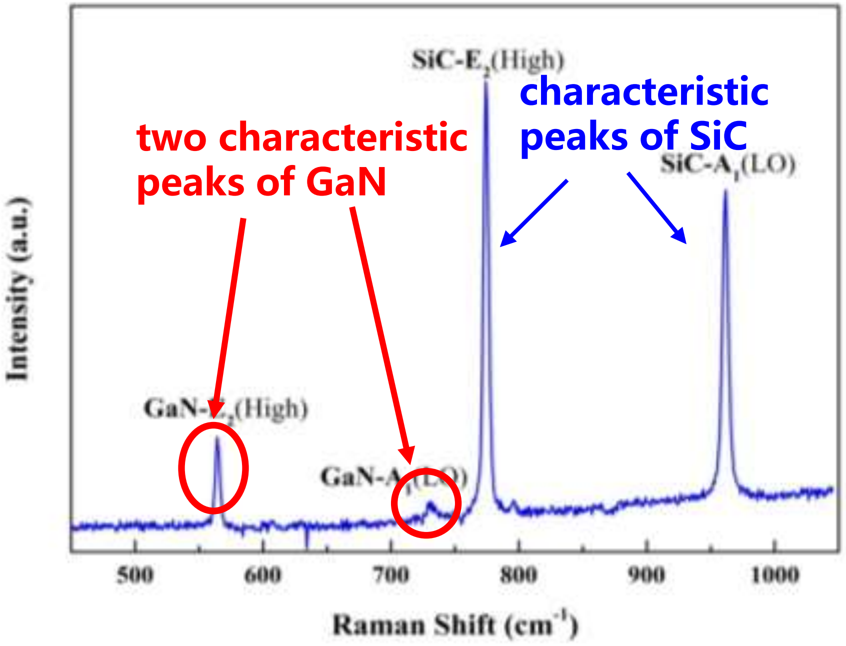
Raman shift of single-wall carbon tube varies linearly with **temperature**
Wang HD *et al.*, *Nanosc Microsc Therm 2013*



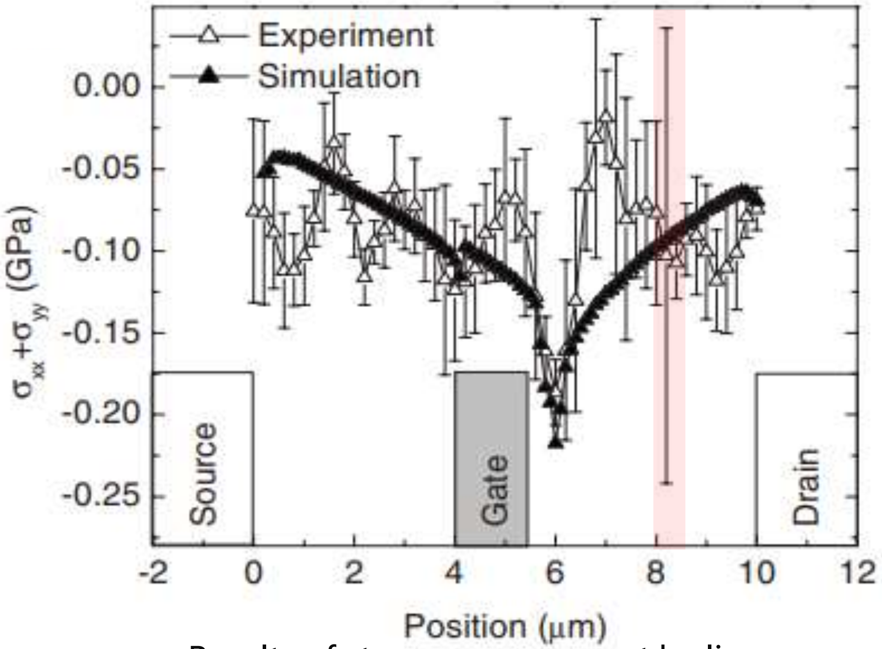
Raman shift of graphene varies linearly with **stress**
Mohiuddin TMG *et al.*, *PRB 2009*

Whether Raman method achieve integrated measurement of multiple physical fields?

Fatal problem of multi-Raman-peak measurement



Raman spectrum of GaN/SiC heterojunction



Results of stress measurement by linear double-peak method，Choi et al., 2013

- Few materials can satisfy the requirement of **simultaneous and accurate measurement of multiple Raman peaks**
- **Inevitable low signal-to-noise ratio Raman peak will seriously affect the measurement uncertainty of the multi-Raman-peak method**

It is necessary to develop a single Raman peak method with strong universality, high accuracy, and high reliability

How to decouple temp. & stress in complex structure

- How to **extract temperature and stress simultaneously** from a device with a **complex stress field** and an **unknown temperature field**? $\Delta\omega = a\sigma + \chi\Delta T$

➢ The **effective Raman temperature coefficients (ERTC)** contain information about **the structural constraints** and thus can determine the **thermal stress**

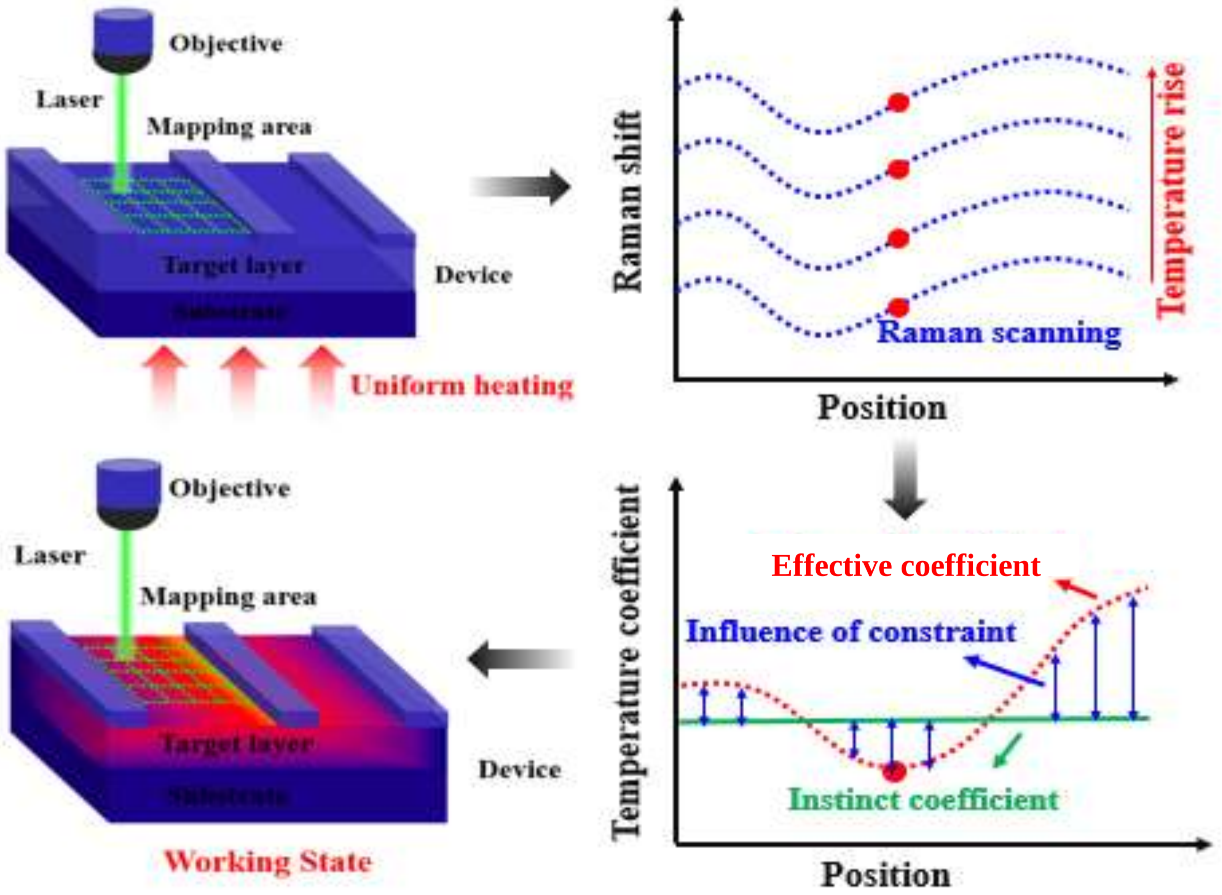
Scan and calibrate the distribution of **ERTC**

↓

Extract **internal constraint** from **ERTC**

↓

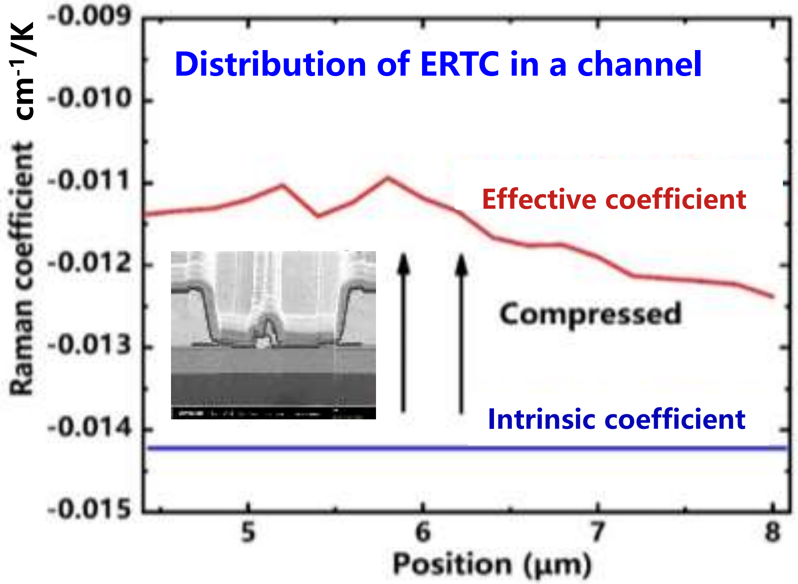
Measure **temperature rise** and **thermal stress**

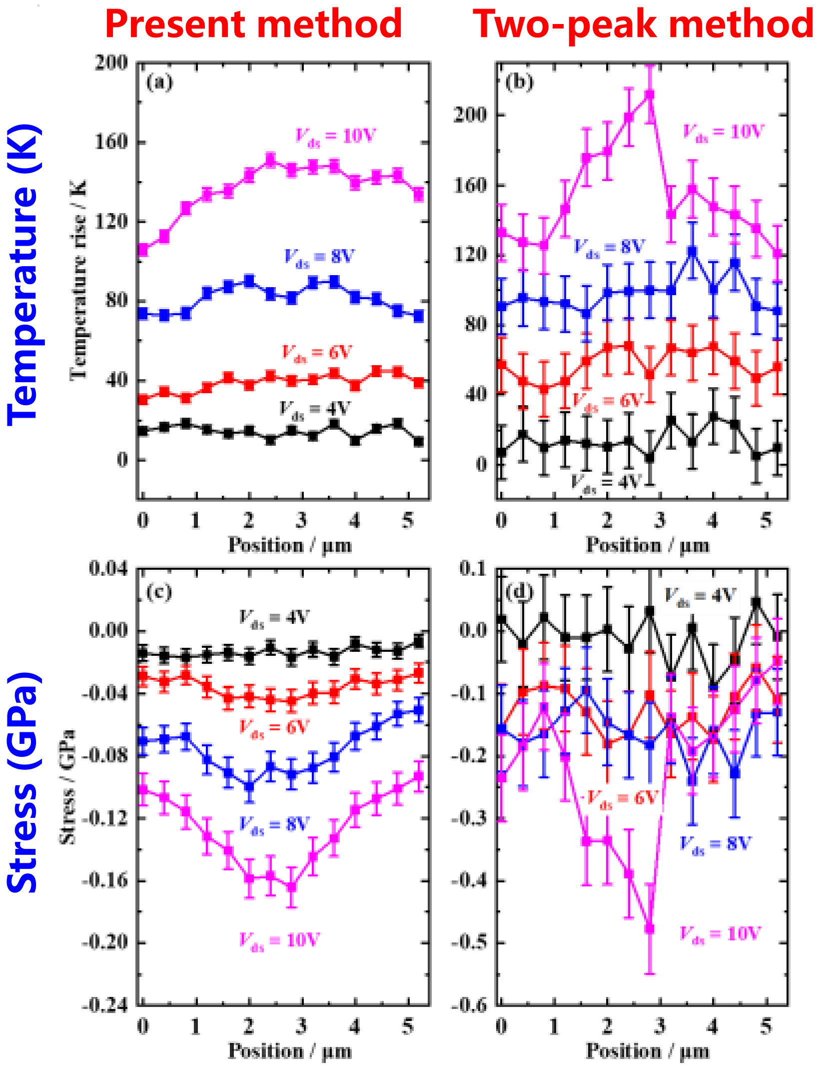


ZL 202210258793.1

Experimental verification

- **Present method** and **double-peak method** were respectively used to analyze **the same Raman scanning data** in the channel of a power device

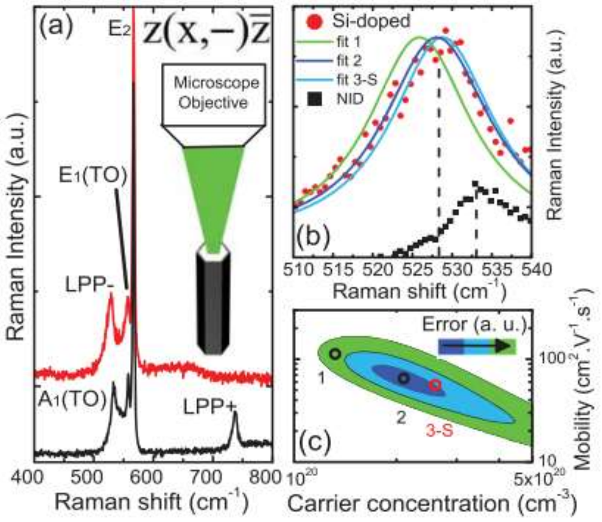




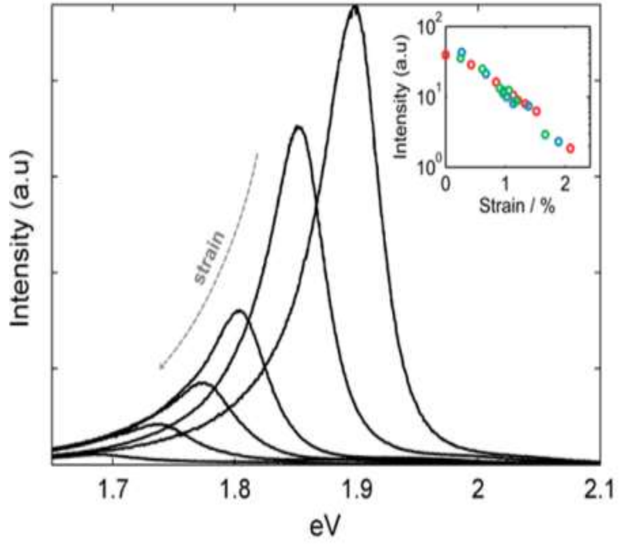
- The **spatial distribution of ERTC is uneven**, reflecting the influence of **constraints.**
- The temperature and stress data measured by the present method **distribute continually and with stronger regularity**, indicating higher **rationality** and **reliability.**

Other combinable optical and electrical methods

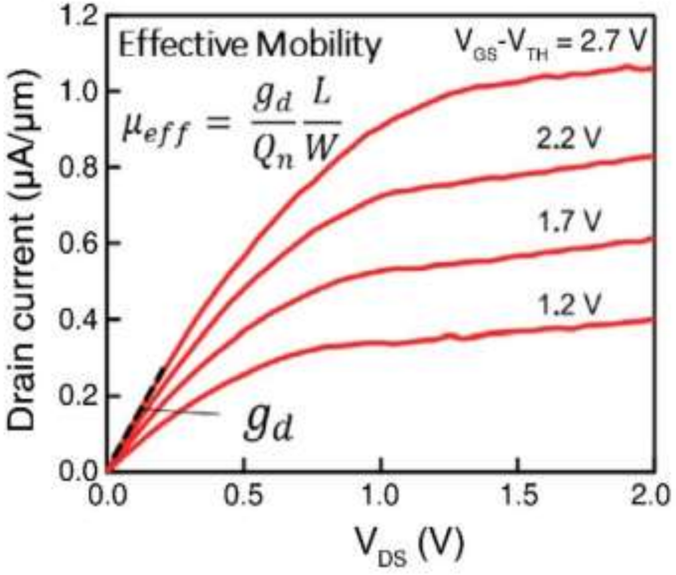
- By analyzing **plasmon coupling modes** and collecting **photoluminescence(PL) spectra**, Raman system can also measure **carrier mobility** and **bandgap**
- Since the properties directly determine the output of the device, the **effective mobility** can be measured by analyzing electrical **I-V characteristics**



Kozawa T et al. Journal of Applied Physics, 1994.



Swan et al. Nano Letters, 2016.



Sekhar Babu Mitta et al 2D Materials, 2021

Relationship between Plasmon mode intensity and frequency:

Some formulas:

$$I = I_0 \frac{n_2}{n_1}\left(\frac{\omega_2}{C}\right)^4 (n_\omega + 1) \cdot A \cdot \mathrm{Im}\left(-\frac{1}{\varepsilon}\right)$$

$$\varepsilon(\omega) = \varepsilon_\infty\left(1 + \frac{\omega_l^2 - \omega_t^2}{\omega_t^2 - \omega^2 - i\omega\Gamma} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_p}\right)$$

The PL peak directly corresponds to the material bandgap:

Unit conversion of bandgap:

$$E_g\,(\mathrm{eV}) = 1240/\lambda_g\,(\mathrm{nm})$$

Expression of the effective mobility:

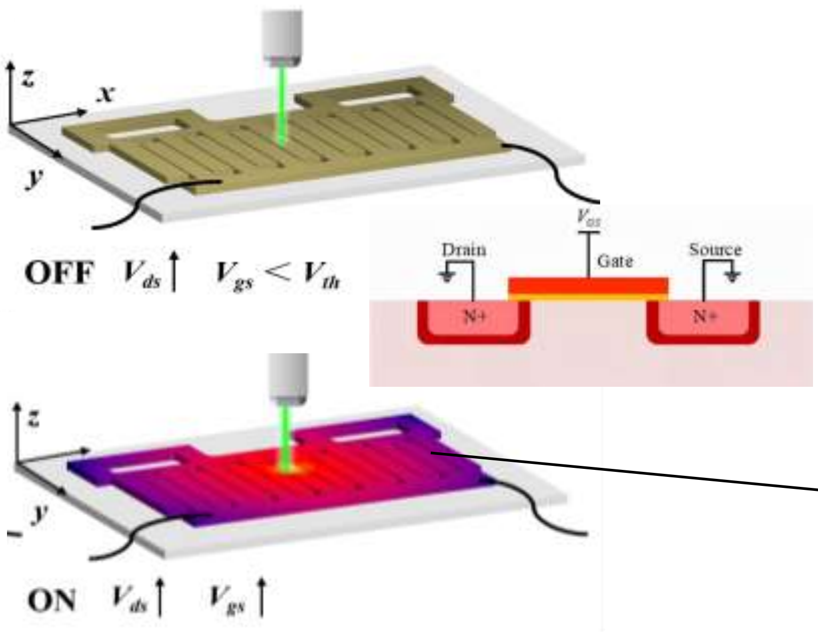
$$\mu_{eff} = \frac{g_d}{Q_n}\frac{L}{W} \qquad g_d \equiv \frac{\partial I_D}{\partial V_{DS}}\bigg|_{constant\, V_{GS}}$$

$$Q_n = C_{ox}\,(V_{GS} - V_{TH})$$

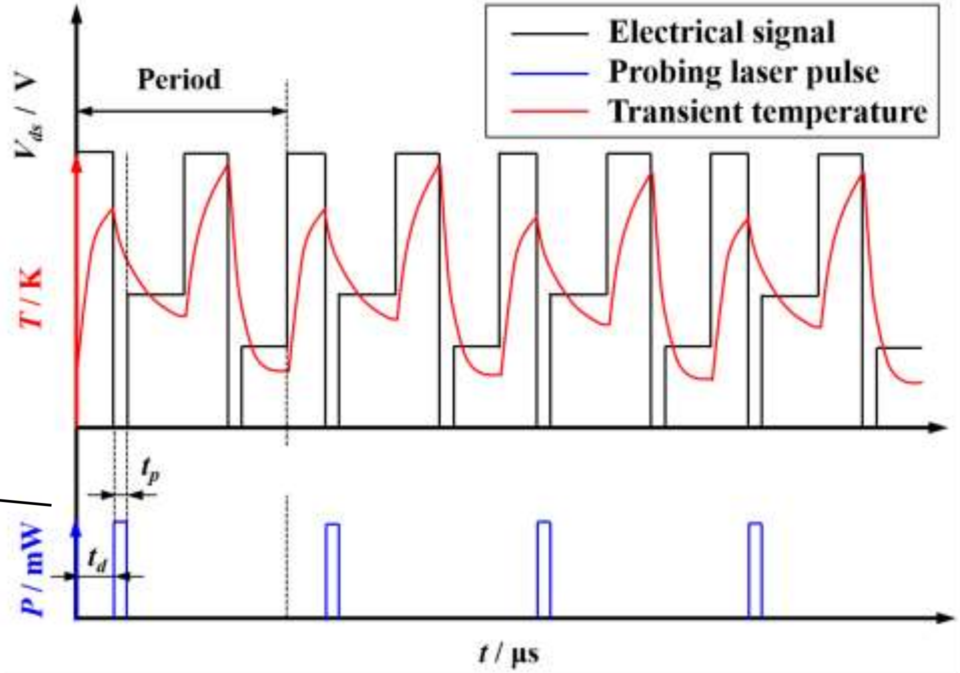
Where L,W is the geometry, Cox is the capacitance

In-situ real-time physics measurement steps

■ In combination with the previously proposed Raman decoupling method, in-situ real-time measurement of multiple physics can be realized



Schematic of the measurement steps

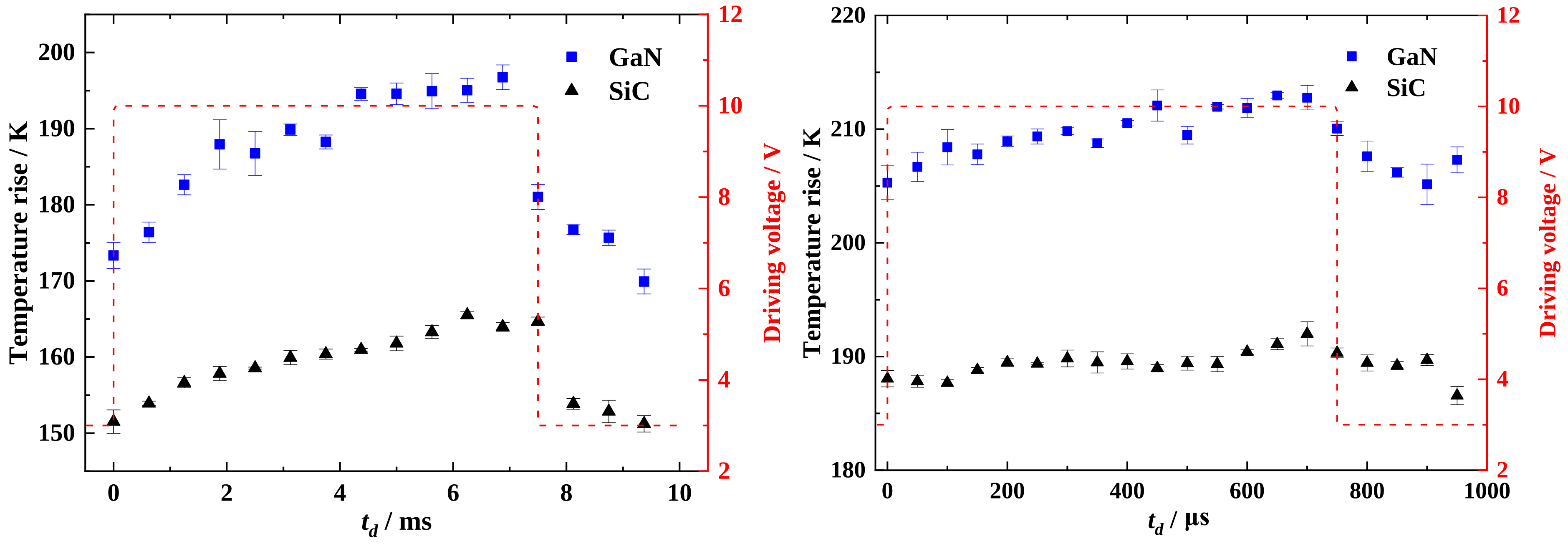


Principle of electro-optic transient measurement method

- ➢ Vgs=0,Vds=0, measure the residual stress; Vgs=0, Vds↑ (OFF) , measure the electric field
- ➢ Vgs>Vth (ON), measure the temperature and thermal stress distribution simultaneously
- ➢ Measure transient variation of multiple quantities by electro-optic modulation method

Experimental verification: Temperature variation

- With the transient measurement system, temperature variation of device loaded with high-frequency periodic signals can be effectively measured



➢ Temperature variation of a GaN/SiC device under periodic pulse signals was obtained. Obviously the temperature variation curve is in good agreement with loading pulse signal.

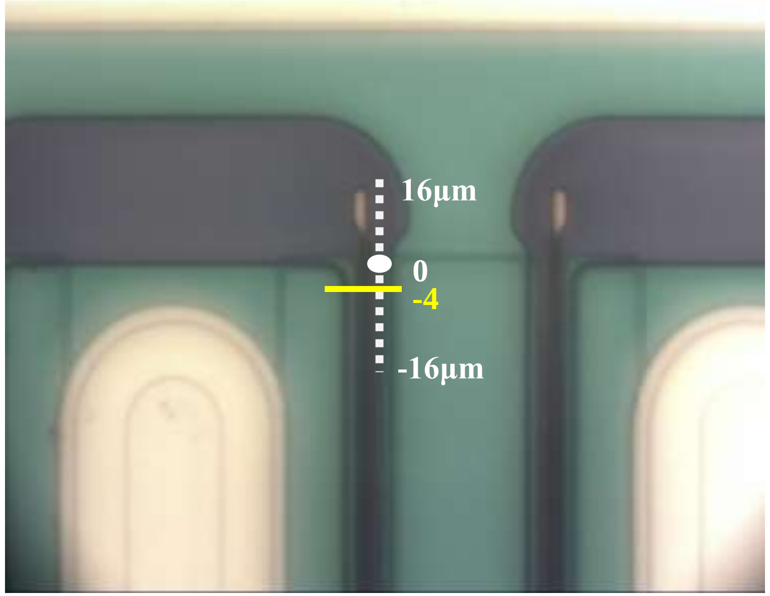
➢ The maximum temperature difference of GaN layer can reach 20K and 10K when the modulation frequency is 0.1kHz and 1kHz respectively (under 3/10V).

Comprehensive Raman-based measurement system

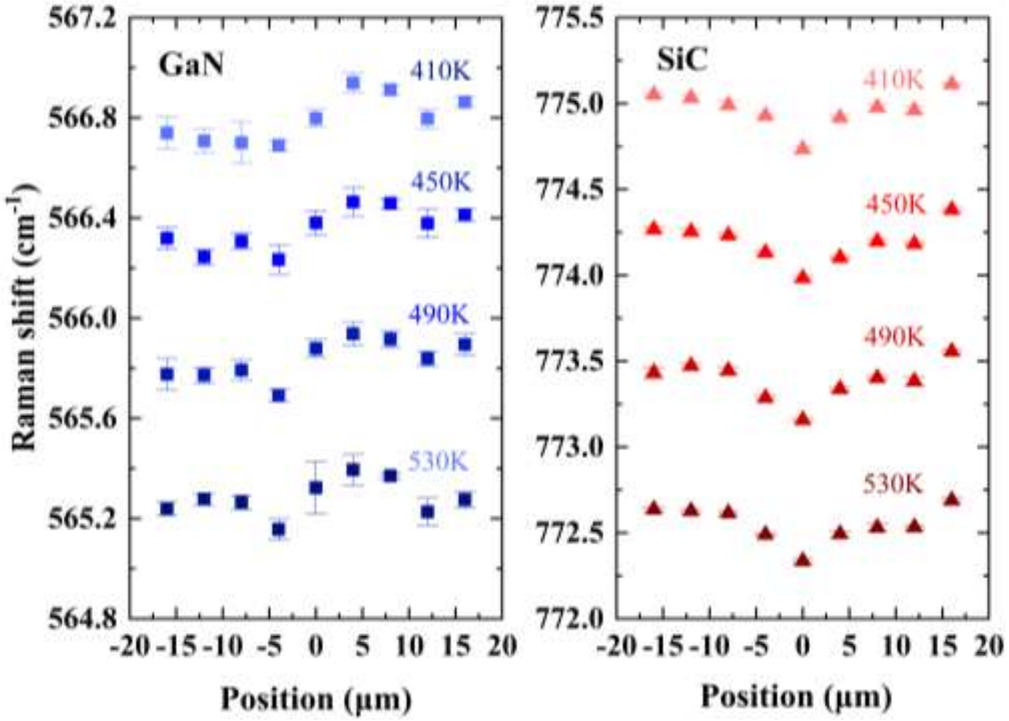
Module	Raman-based method	Information	
Device	Original ◆ Single-Raman-peak method Original ◆ Electro-optic modulation method ◆ I-V Characteristic method	• Residual stress • Temperature • Thermal stress • Electric field • Transient multiple quantities	Field
Material	Original ◆ Dual wavelength flash method ◆ Plasmon fitting method ◆ PL peak method	• Effective mobility • Thermal conductivity • Interface thermal resistance • Carrier Mobility • Carrier Concentration • Dielectric constant • Bandgap	Properties

Residual stress distribution of the device

- By **Raman peak position scanning**, the **local stress distribution** at the edge of the device was further studied



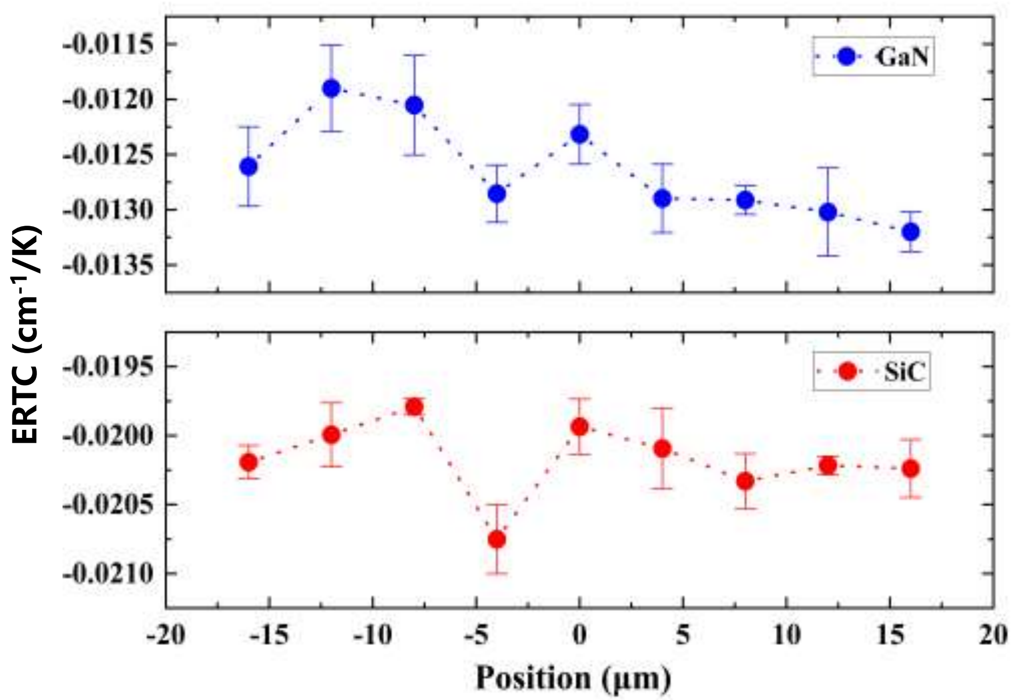
Scanning position of the device

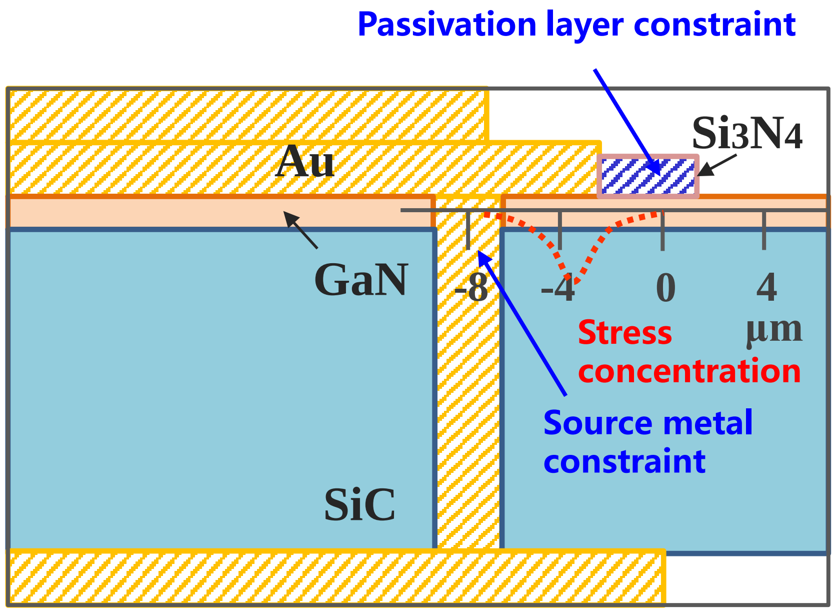


- **Relative difference of residual stress** at the scanning range **can be up to 0.15GPa (Tensile).**
- **Residual stress is almost intact inside the device** in the process of temperature change, which may cause effects on the device that is **hard to eliminate.**

Device structure causes stress distribution

- Stress concentration points and corresponding structural constraints are in good agreement, indicating that structure plays a decisive role in stress distribution



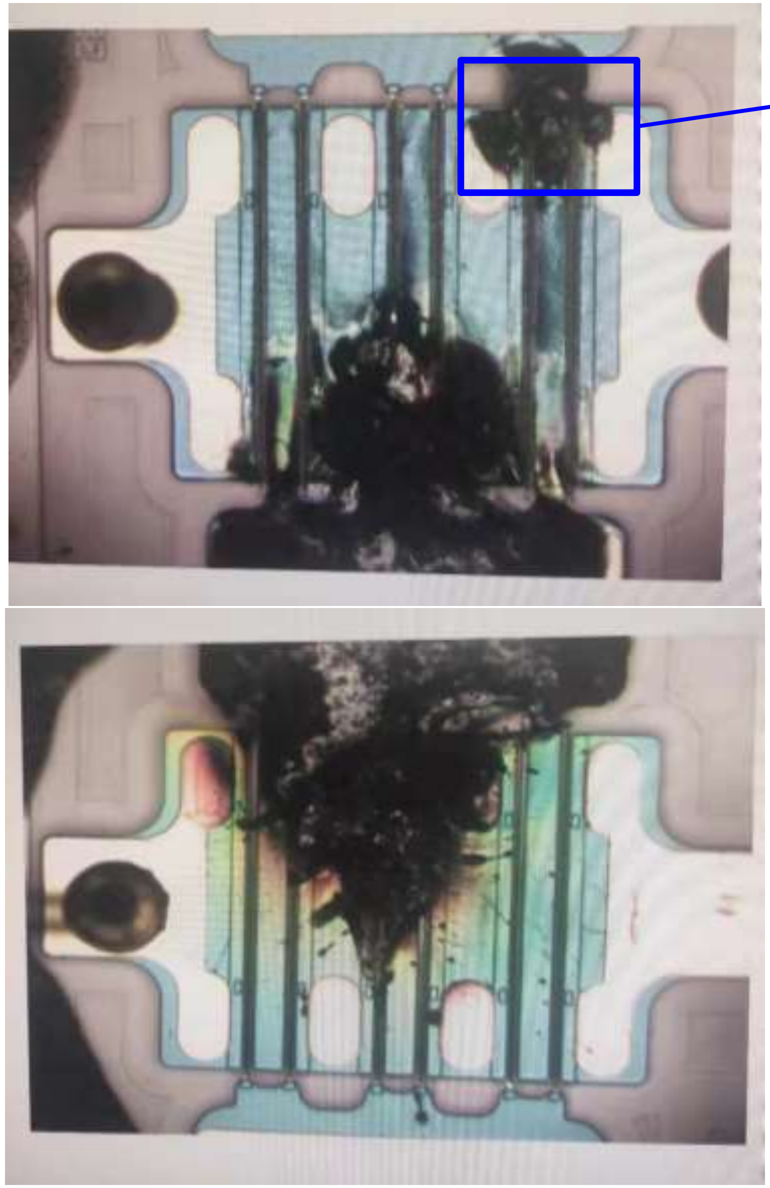


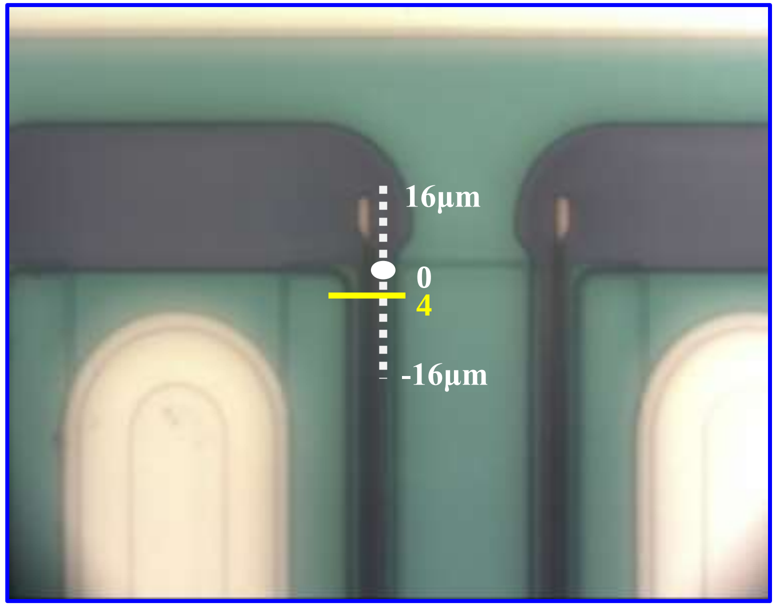
diagrammatic cross-section of the device

> There are obvious constraints at x=0μm and x=-8μm positions, resulting in compensation expansion at x=-4μm, which is consistent with the stress concentration point measured.

Structural design can directly change the stress distribution and is expected to become a new approach for overall device optimization

Tensile stress concentration leads to device damage

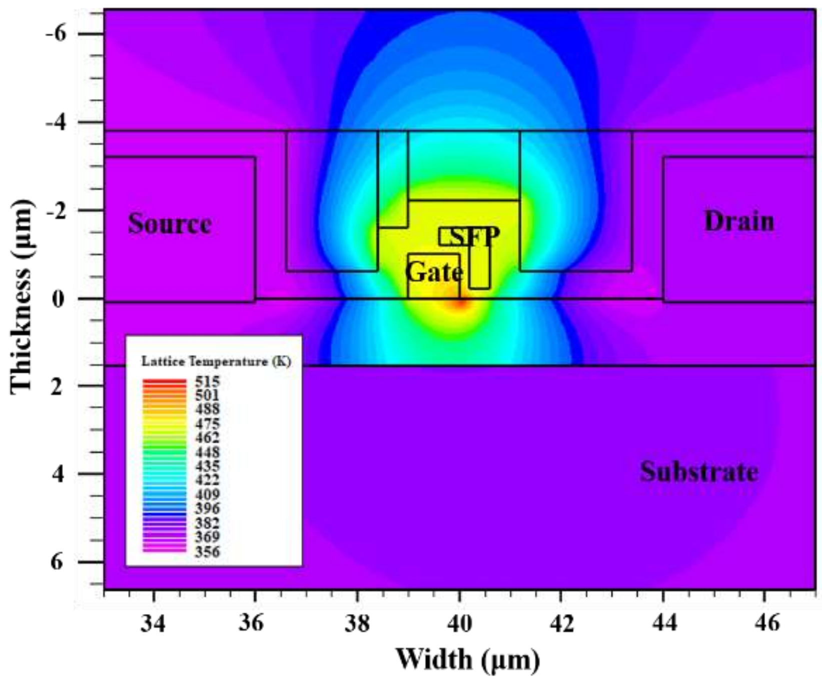




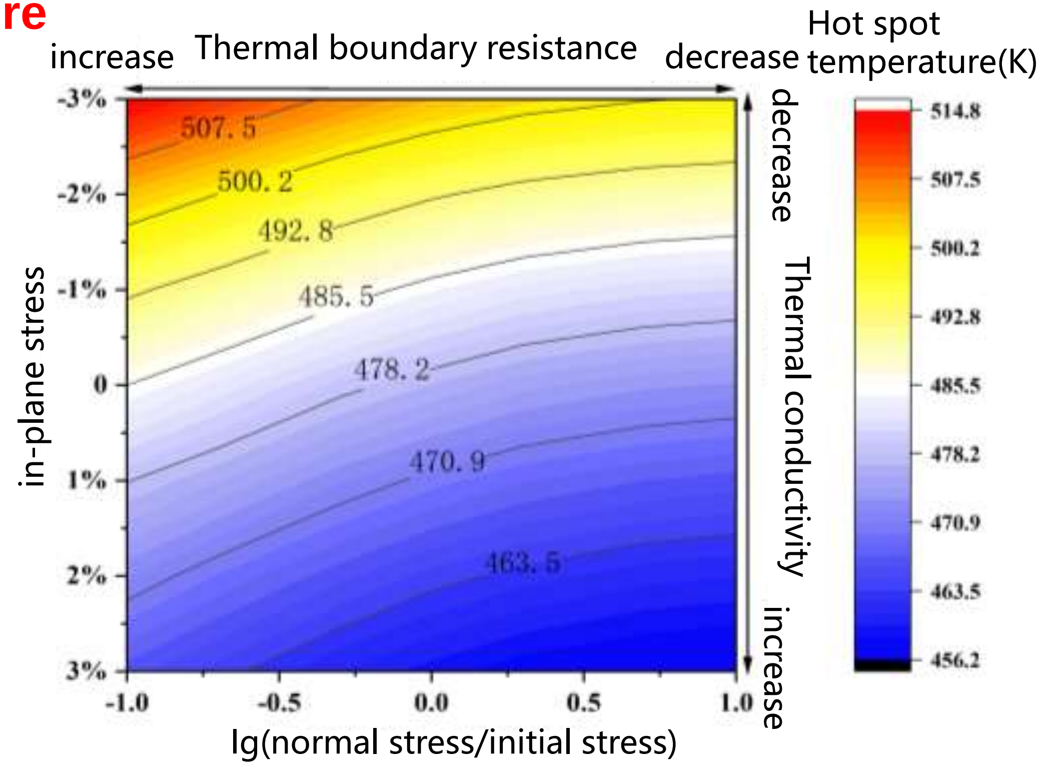
- **Local tensile stress may lead to:**
  - **Bigger power consumption**
  - **Worse heat dissipation performance**
  - **Lower ultimate temperature**
- **Study of multi-physical coupling mechanism can provide important guidance for device failure mechanism analysis and future structural optimization design**

Effect of stress-coupling thermal properties on device

- Simulation: For a single transistor, stress can cause thermal properties to change, then has a significant impact on the hot spot temperature



Isotherm diagram of single GaN-based transistor (simulation results)



Variation of hot spot temperature under the joint action of in-plane and normal stresses

- By regulating the normal stress (1/10 to 10 times) and in-plane stress (-3% to 3%), the interface thermal resistance and thermal conductivity of the heating layer in the transistor significantly change, and the hot spot temperature can change above 50 K
- Verify the necessity and importance of multidisciplinary integration optimization

Safety issues limit the application of LIBs

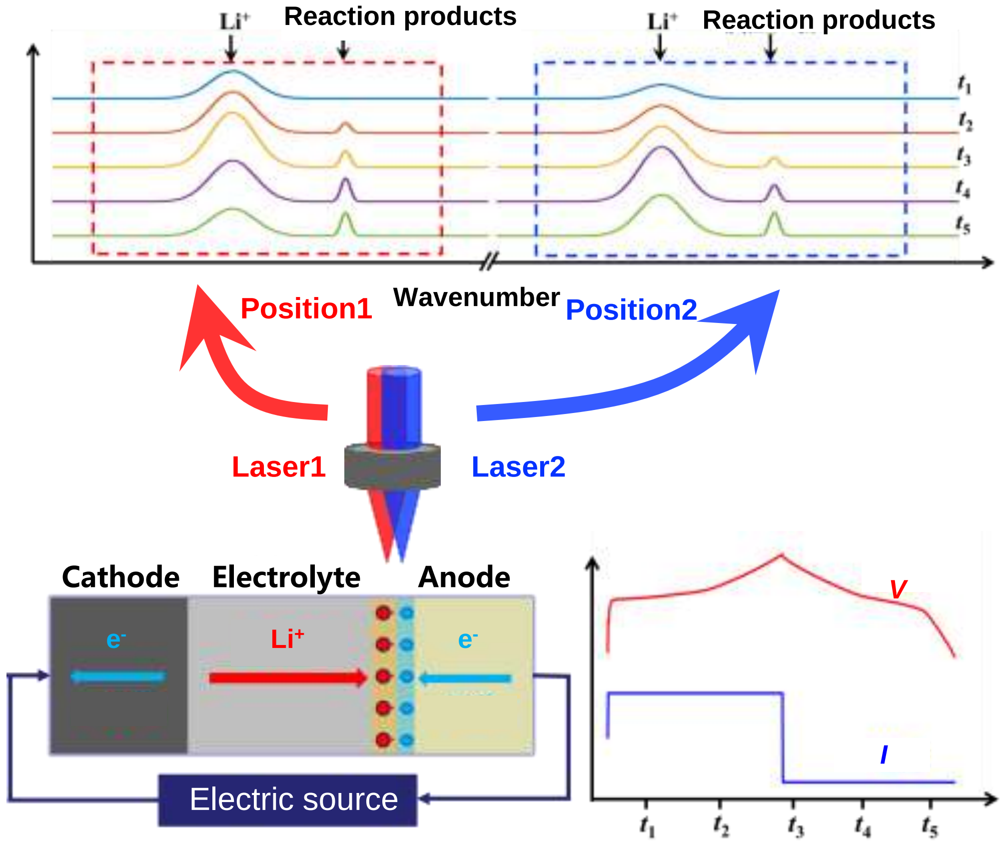
- Liquid lithium-ion batteries(LIBs) has serious safety issues

Mobile phone fire-prone

All-electric car caught fire

- All-solid-state LIBs using non-flammable solid electrolytes are promising options for electric vehicles and portable electronic devices, due to their significantly better safety characteristics and higher energy densities
- A stable electrode-electrolyte interface is a key to high energy density all-solid-state LIBs, but the nanoscale behavior of the interface is not well understood
- Need to develop an effective measurement method

Dual wavelength electro-optical Raman method



Raman

Peak intensity: Ion concentration

New peak: Reaction products

+

DW

lag between two positions:

Peak intensity: Ion transport

New peak: interphase reaction

+

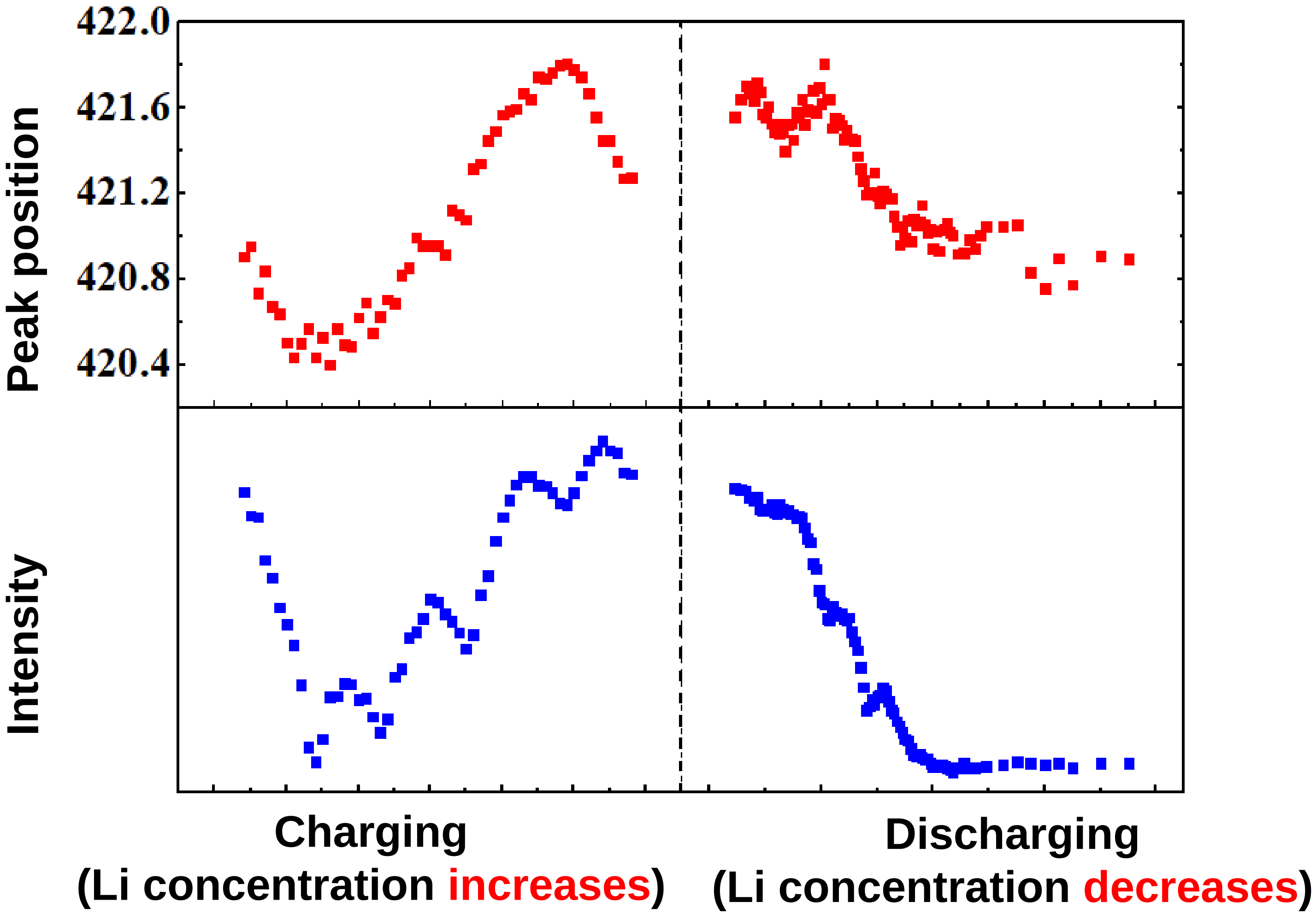
electro

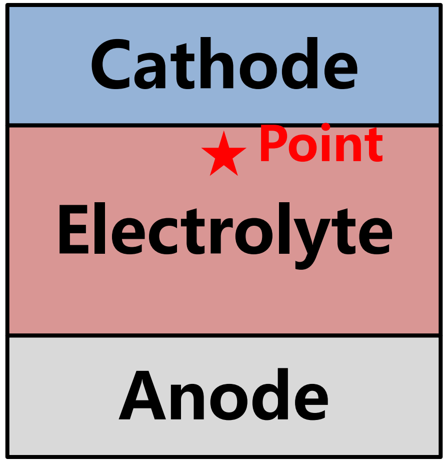
Ion-electron coupling transport

In situ and real-time detection of the interface reaction and ion-electron coupling transport

Lithium-ion concentration at interface

➢ **Synchronous changes in Raman peak intensity and peak position with lithium ion concentration**

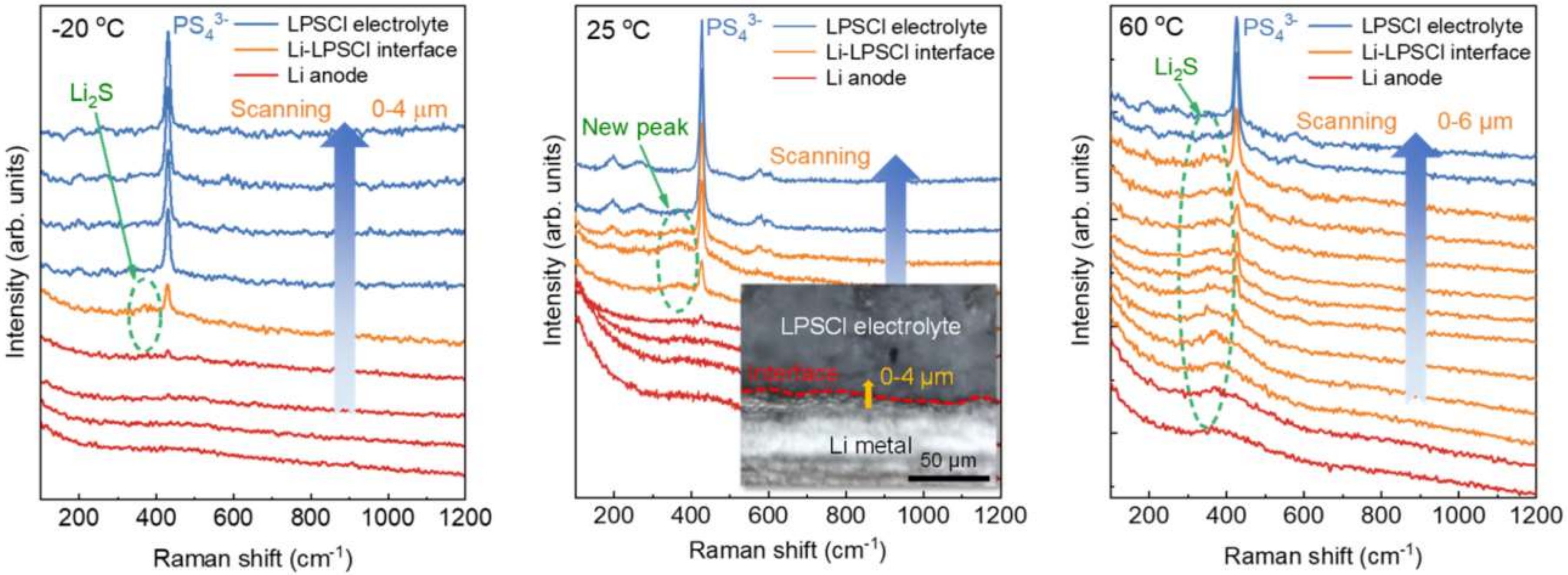




Dynamic monitoring of SEI

➢ Raman spectra of anode interphase versus temperature

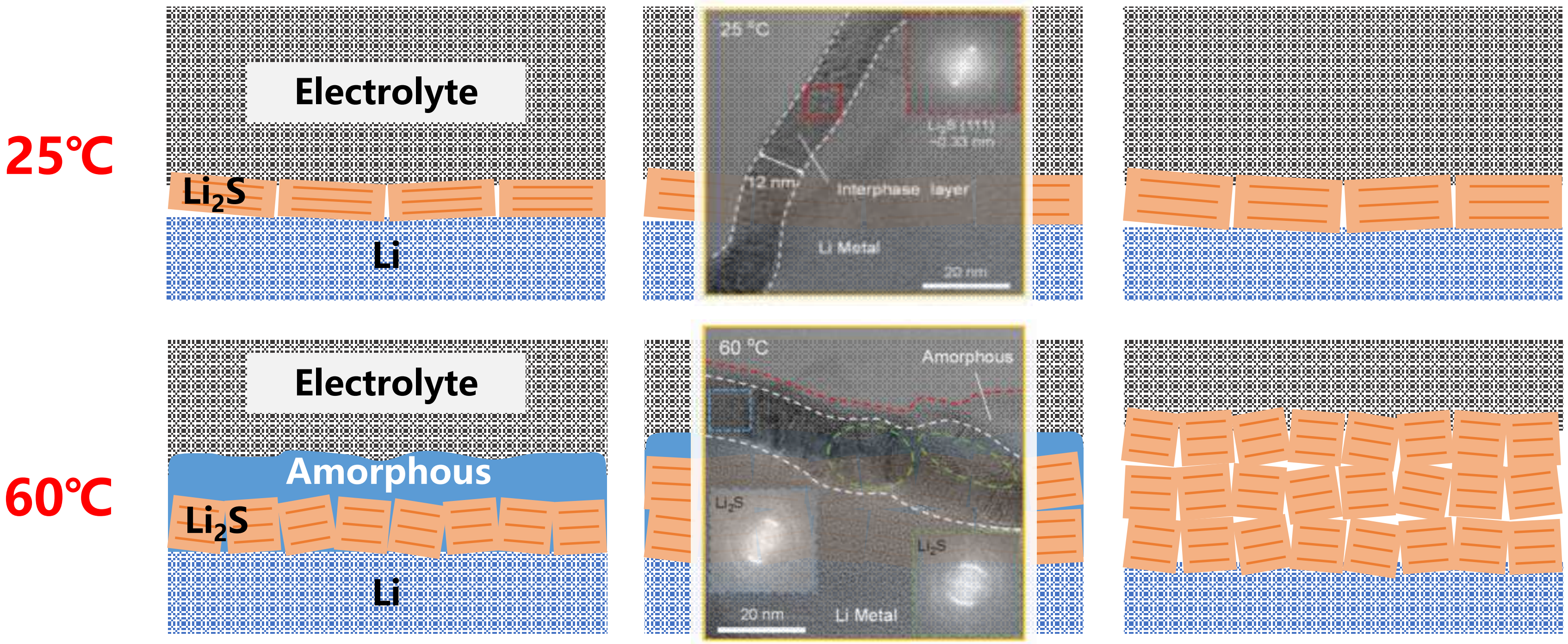
-20 ℃ 25 ℃ 60 ℃



◆ New peak at ~372 cm^{-1} suggests the formation of Li_2S

◆ As temperature increases, solid electrolyte interphase (SEI) gradually thickens, indicating the intensification of interfacial reactions

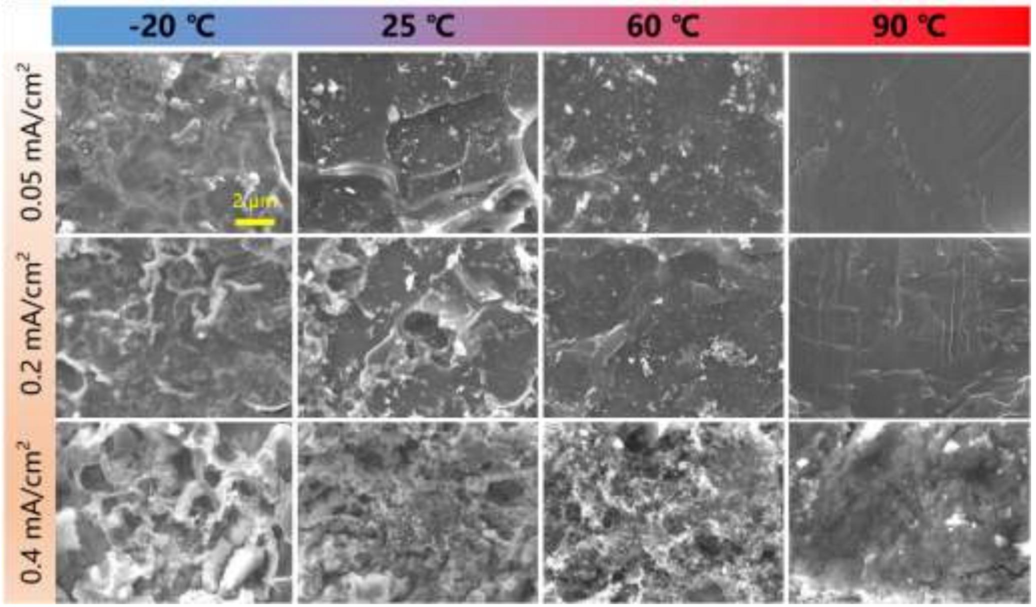
Mechanism of Interface Reaction



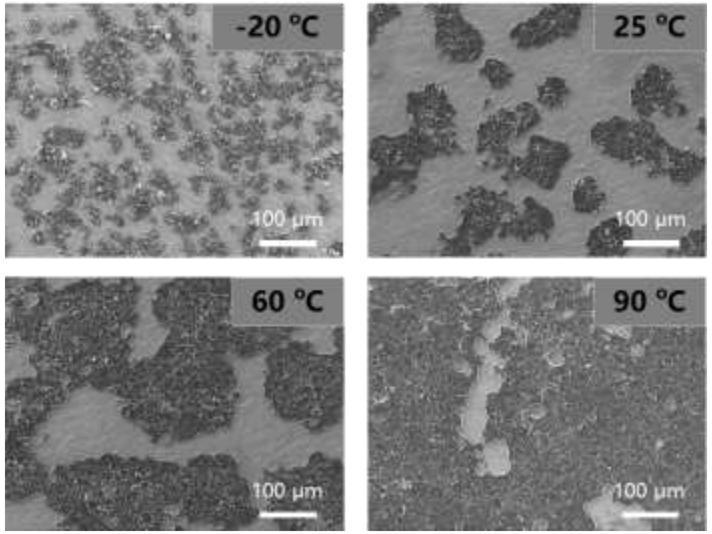
- ◆ At 25 °C, a single-crystal Li_2S layer with ~12 nm thickness is formed at 25 °C with good passivation on the interface
- ◆ While at 60 °C, the interphase is composed of polycrystalline Li_2S accompanied by a disorder−order phase transition.

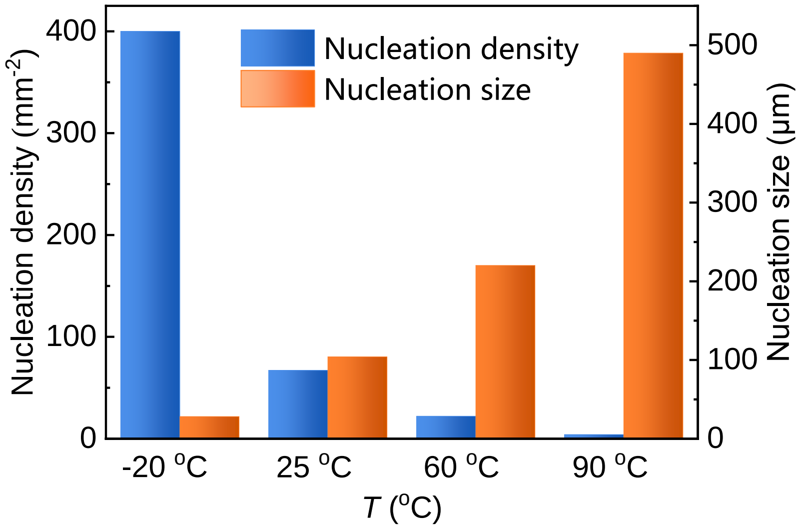
X. Zhang et al. ACS Energy Letters, 2022, 7：3064-3071

Temperature effect on deposited Li

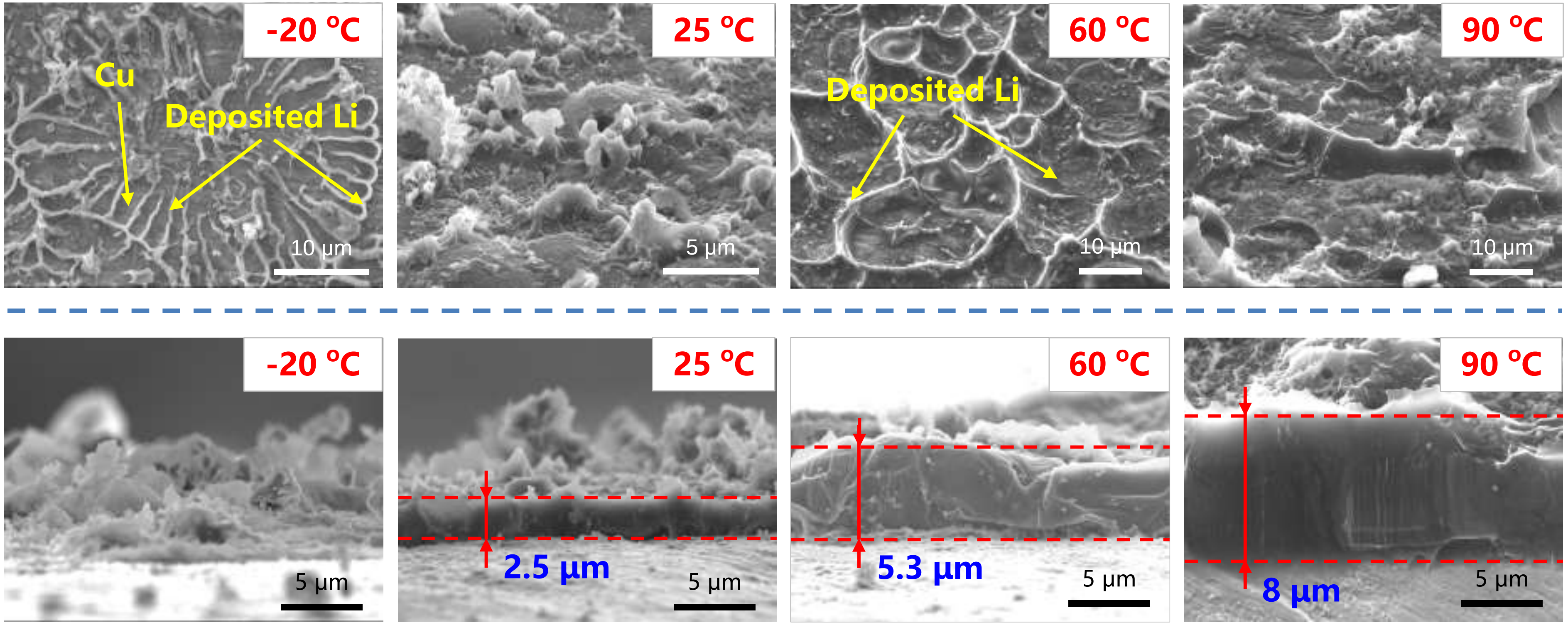


- ➢ **Smoother surface morphology at increased temperature and decreased current**
- ➢ **Larger nucleation size and lower nucleation density at elevated temperature**



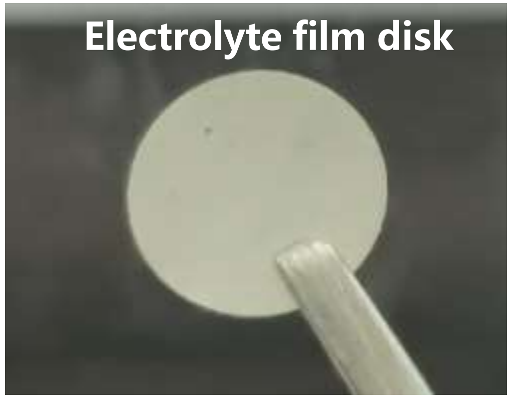


Temperature effect on deposited Li

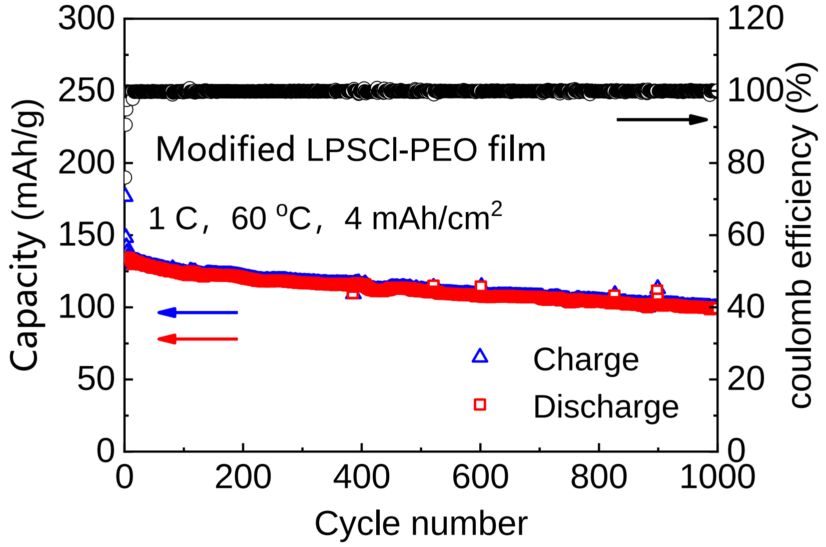


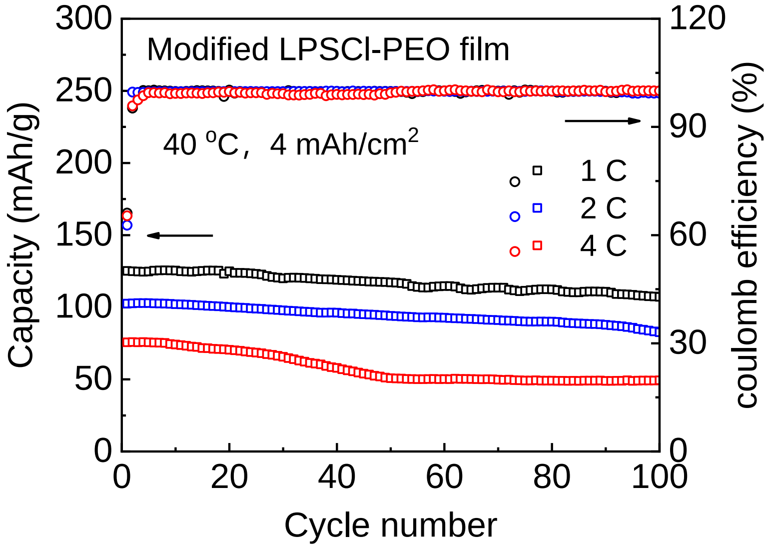
- With the temperature increasing, the deposited Li changes from vertical growth along the voids and grain boundaries to lateral deposition on the electrode surface, inhibiting the growth of lithium dendrites

Modified sulfide electrolyte film



◆ The electrolyte thickness decreased from ~1000 μm to 65 μm



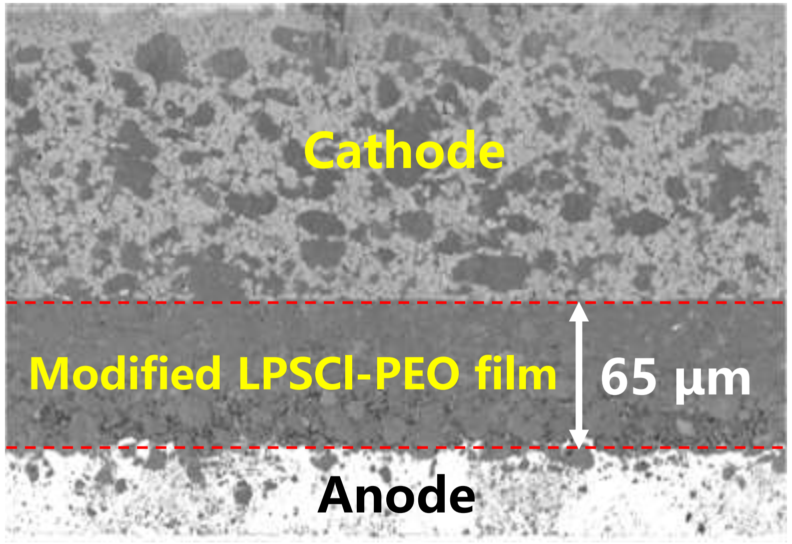


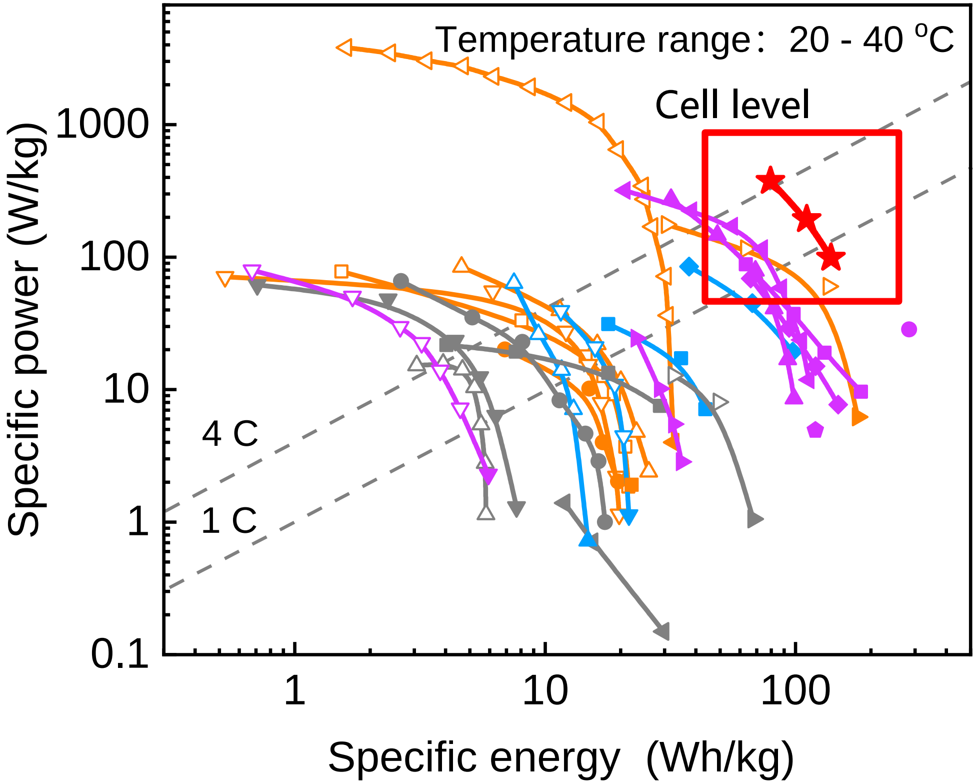
◆ Stably cycled at 1C over 1000 cycles

◆ Stably cycled at 4C with 75 mAh/g capacity

Modified sulfide electrolyte film

Cross section after 1000 cycles





- **The cell still maintains a quite stable structure after 1000 cycles**
- **The specific energy and power of the cell with modified electrolyte film are increased by 1 order of magnitude**

X. Zhang et al. Journal of Power Sources, 2021, 485: 229325

Early diagnosis and screening of cancer is important

➢ Cancer is a major public health problem that seriously threatens human life

Early Diagnosis Techniques

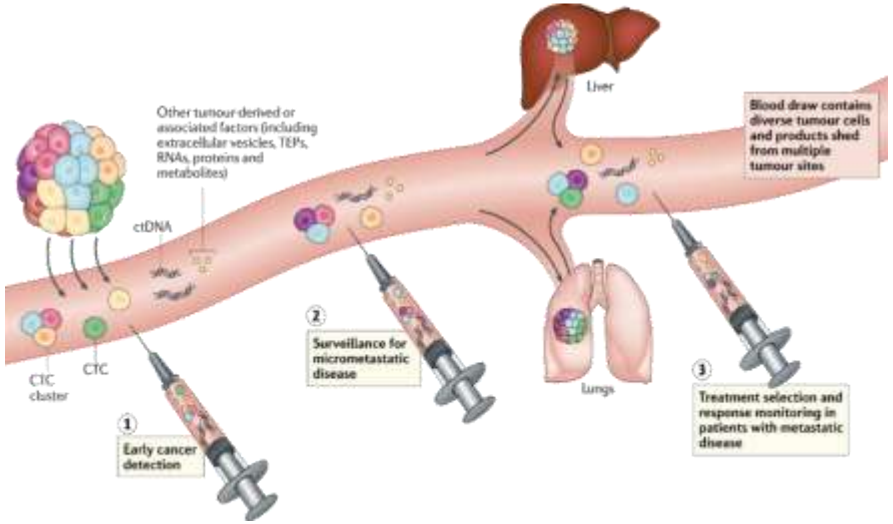
Based on tissue imaging

Gastrointest. Endosc., 96(3): 402-410 (2022)

Relying on doctor's experience, lack of objectivity

Early screening technology

Based on liquid biopsy



Nat Rev Clin Oncol, 18: 297-312 (2021)

Limited markers, limited specificity, and high cost

Needs and challenges of cancer research

Challenge

New detection methods

Early Diagnosis Techniques

Early Screening Technology

Objective and sensitive

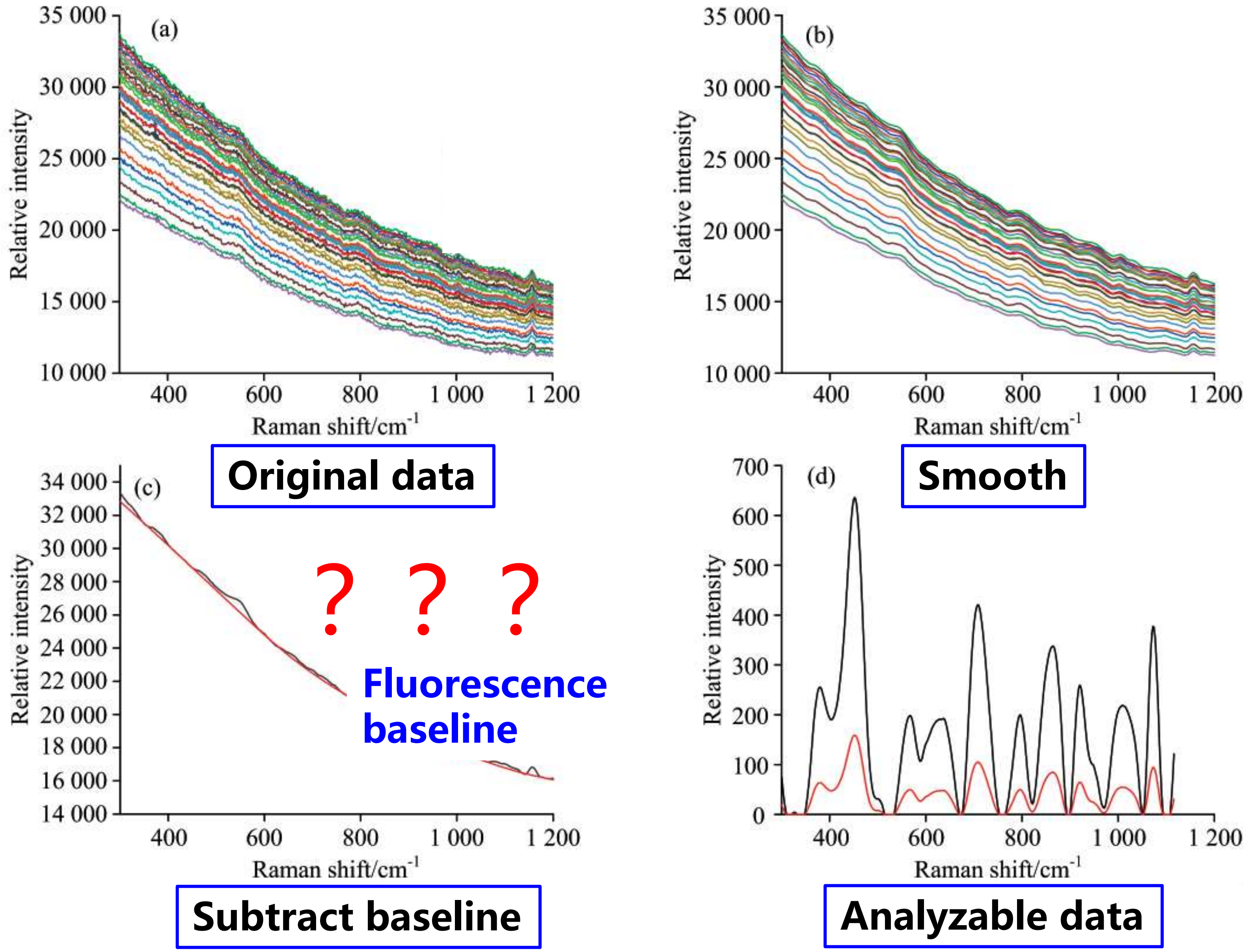
Label-free and cost-effective

Raman

Molecular-level high-precision characterization technology

Beneficial for mechanism research

Limitation for bio-Raman test

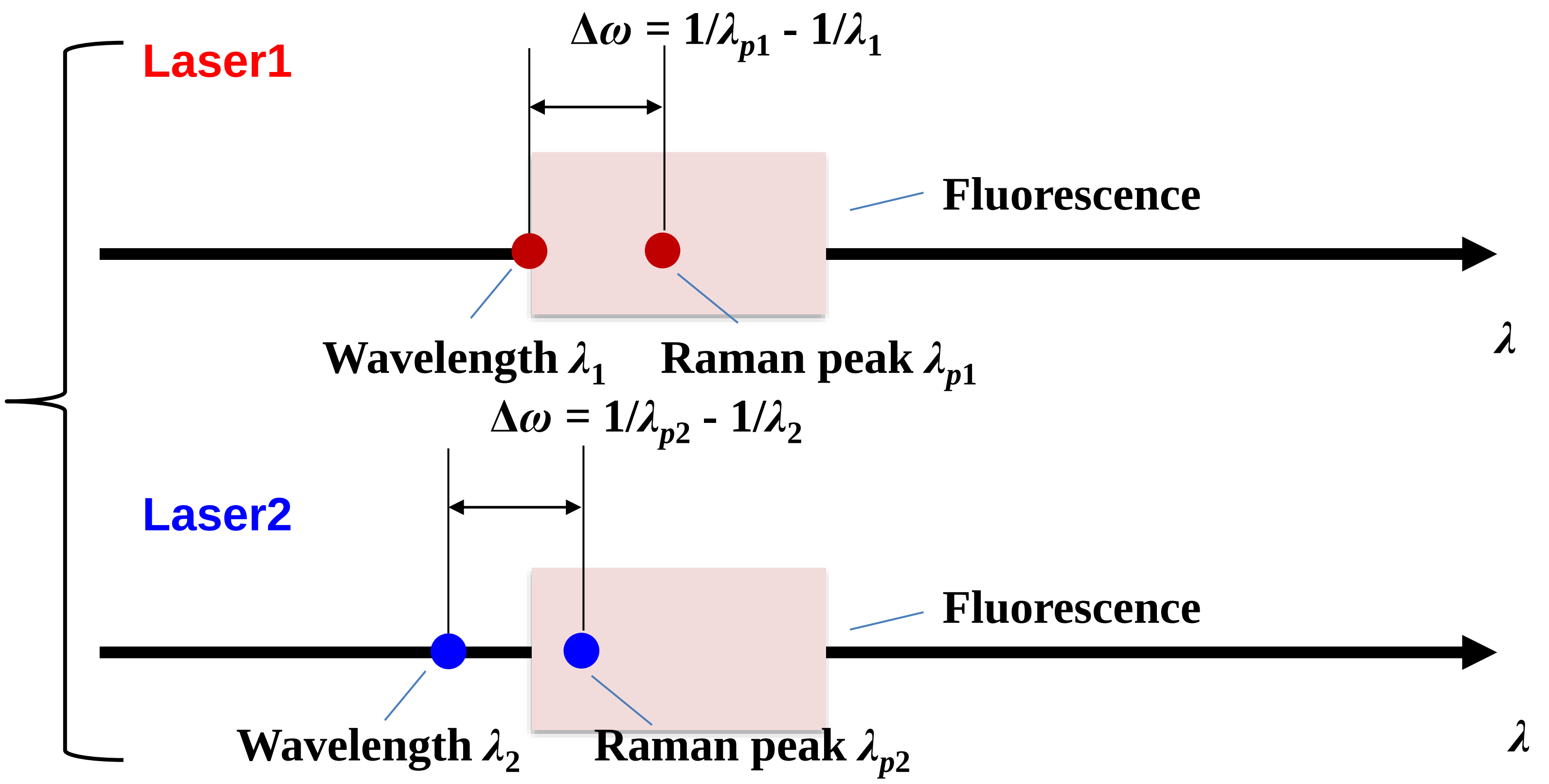


Fluorescence elimination by dual-wavelength Raman spectroscopy

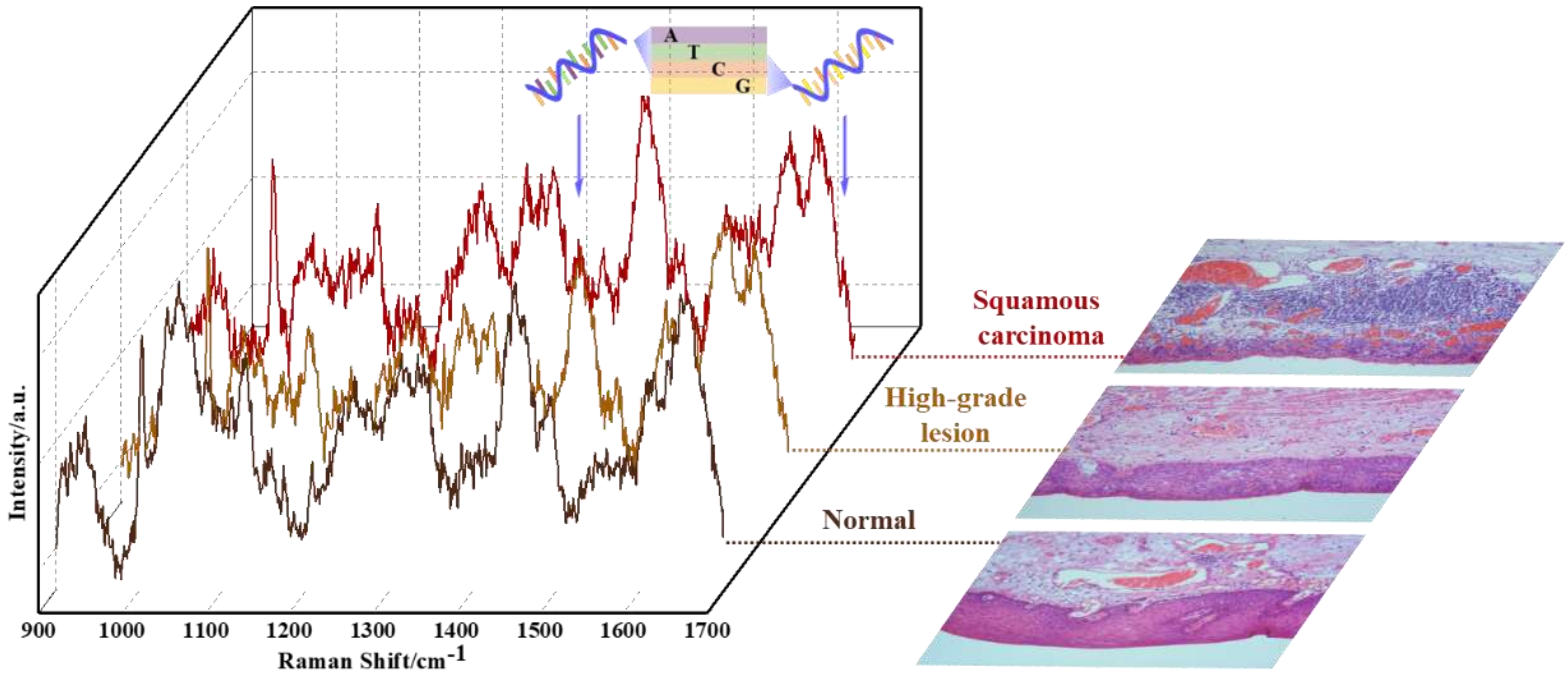
- **Fluorescence:** electron absorbs energy and emits fluorescence, its wavelength independent of incident light
- **Raman:** Inelastic scattering generated by energy exchange between molecules and incident light, its wavelength relate to incident light

Compare

Eliminate fluorescence



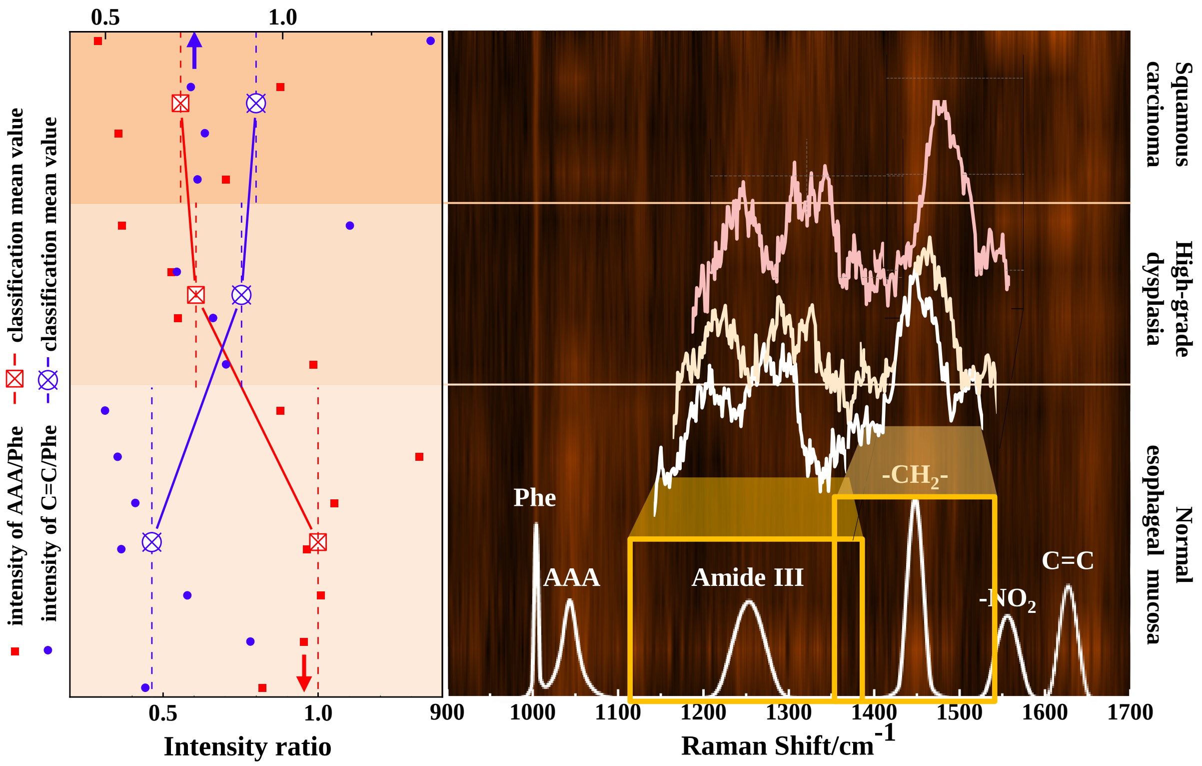
Detection results of esophageal tissue



New peak: the potential Raman diagnostic criteria → Nuclear increase

- ✓ **1368 cm^{-1}: represented the scissoring (in-plane bending) mode of $C5H_3$ in adenine (A), thymine (T), and cytosine (C)**
- ✓ **1685 cm^{-1}: the stretching mode of the C2=O bond in cytosine (C), the stretching mode of C6=O in guanine (G), and the bending mode of $N1H_2$ in guanine**

Detection results of esophageal tissue



Phe: phenylalanine

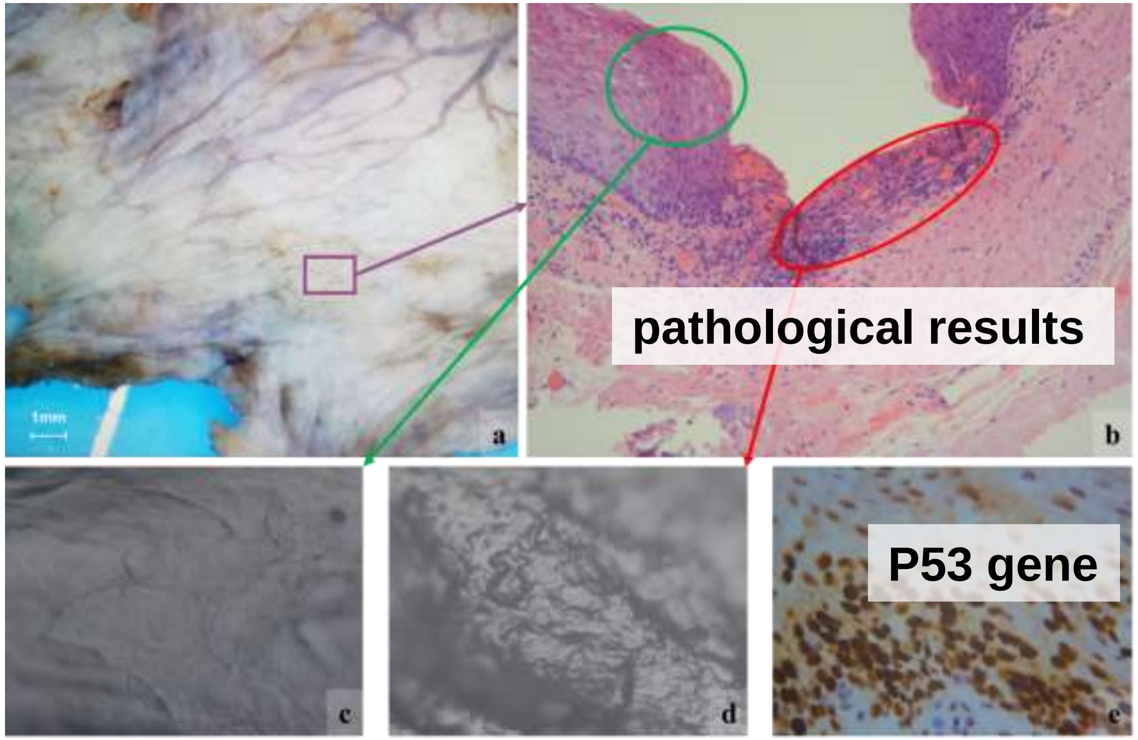
AAA: aromatic amino acid

- **The content of amide III increased in the squamous carcinoma stage**
- **The content of methylene in lipids and proteins showed similar variations**

Early cancer: Significant changes in the function of proteins and lipids

- **Which can only be determined by Raman rather than a Mass spectrometer**

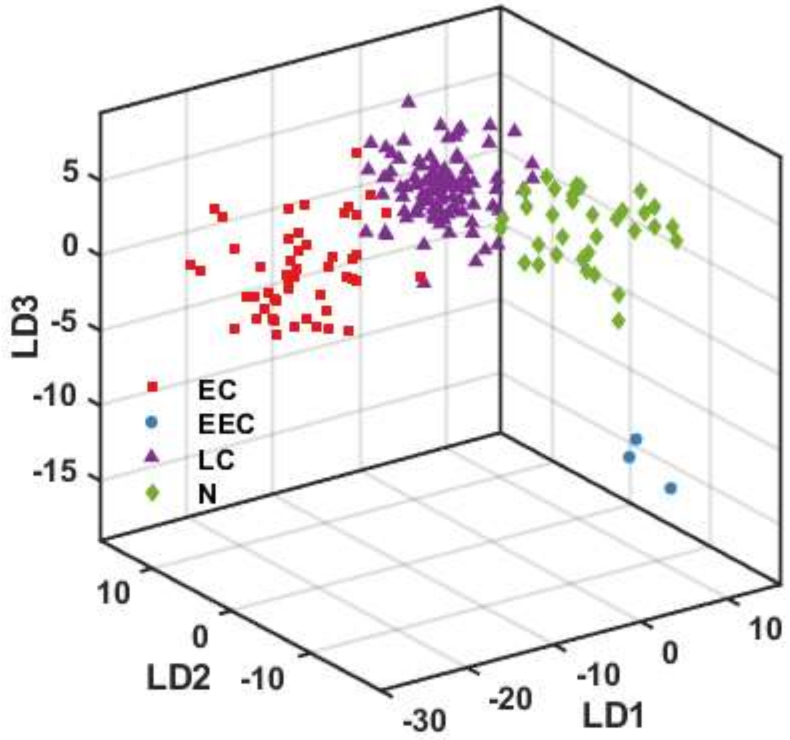
Application in Raman tumor imaging

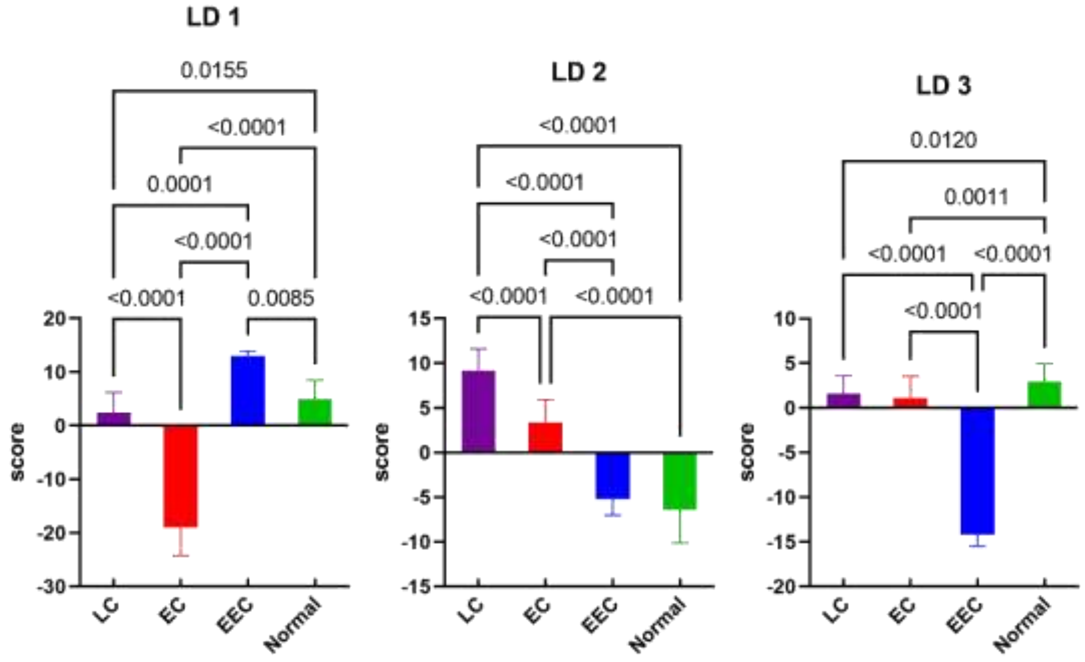


- The imaging results confirmed that the sample had early cancer, providing an accurate area, while the pathological results of this imaging region were indefinite for neoplasia/dysplasia, which will need to be further diagnosed. However, the immunohistochemistry further confirmed mutant p53 gene expression, resulting in the patient being diagnosed with esophageal squamous cell carcinoma, which verified the objectivity and accuracy of this method.

Early Screening Technology

- Sample type: lung cancer(LC) + esophageal cancer(EC) + early esophageal cancer(EEC) + normal(N)
- Cancer warning can be achieved
- Indicate the possible location of cancer, with a small sample prediction accuracy of 100%

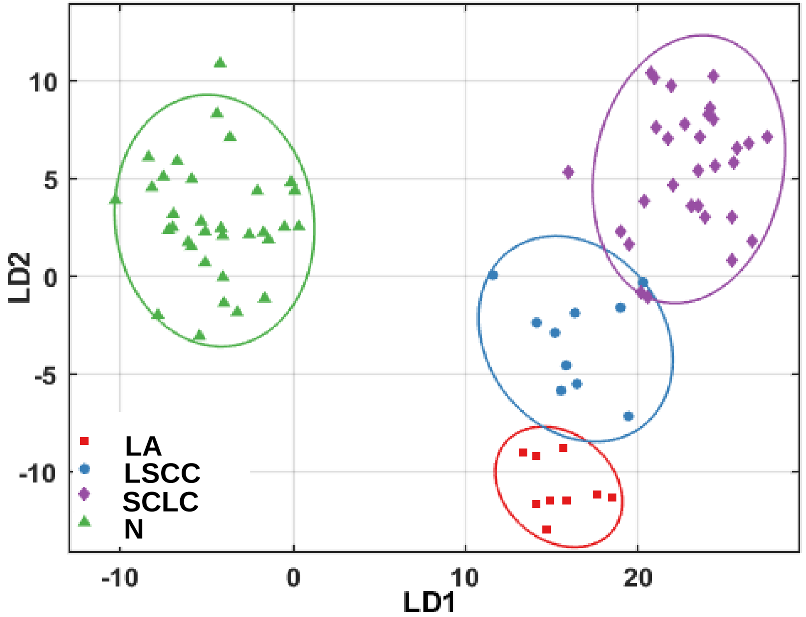




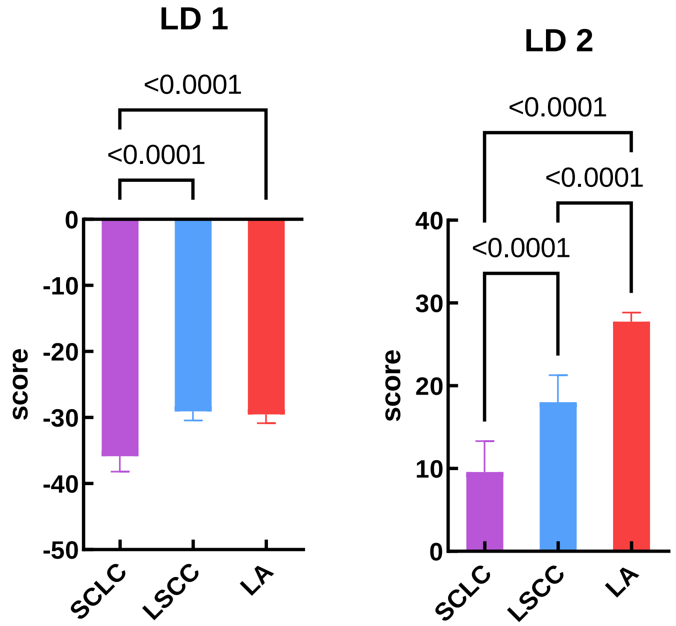
LD1	LD2	LD3
Cancer Classification	Advanced Cancer Warning	Early Cancer Warning

Cancer classification

- Differentiate cancer types originating from different cells
- Significantly distinguished 3 types of lung cancer: small cell lung cancer（SCLC）, adenocarcinoma（LA）, and squamous cell carcinoma（LSCC）



PCA-LDA analysis



Significance test

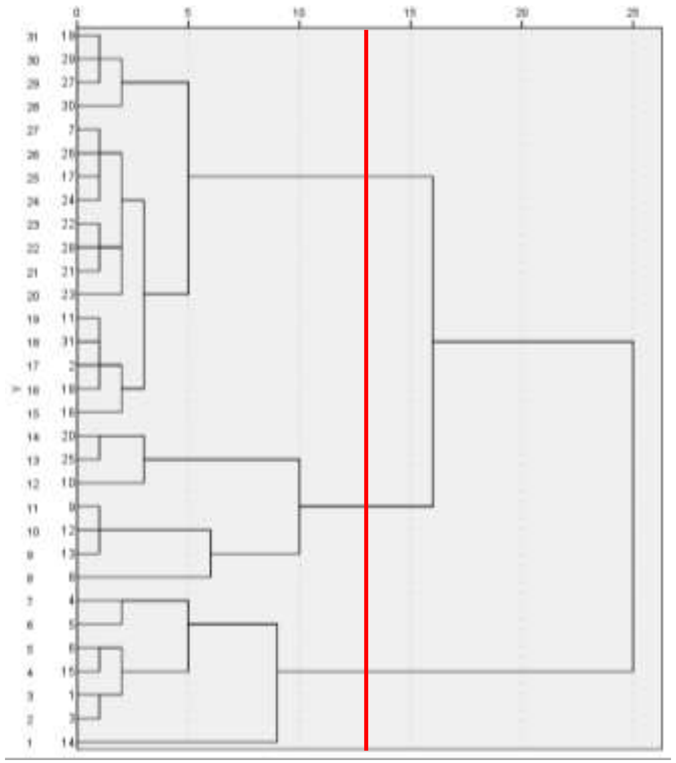
① LD1: has statistical significance in distinguishing SCLC, cancer, and normal;

② LD2: has statistical significance in distinguishing 3 types of lung cancers.

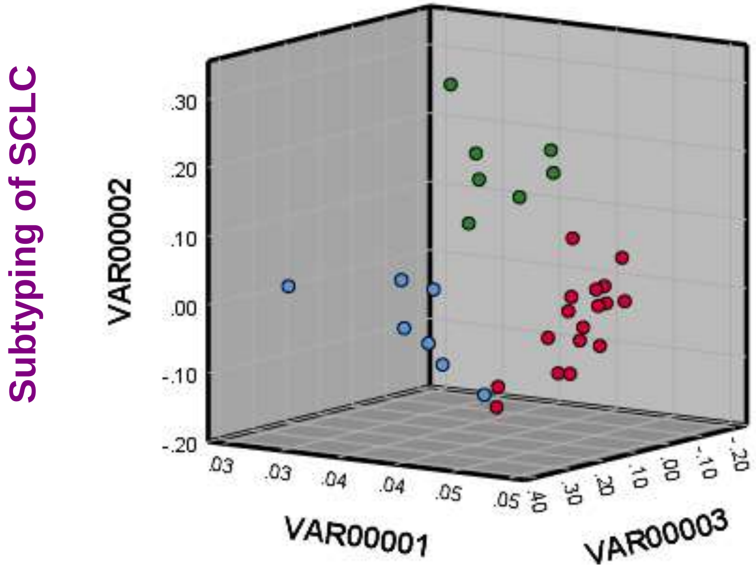
Specificity, sensitivity, and accuracy are all 100%

Subtyping of SCLC

- Subtyping of SCLC contributes to clinically targeted treatment of patients
- In clinical practice, the classification criteria are not yet clear, and subtype classification is still controversial



Hierarchical clustering Results of 30 SCLC Raman Spectra



- Found subtyping criteria of SCLC based on Raman measurement
- Provide a new idea for breaking through the limits of medical research

Conclusions

Be practical as well as generous in your ideals. Keep your eyes on the stars, but remember to keep your feet on the ground.

– Theodore Roosevelt

New challenges in multi-disciplines

- Power device
- Battery
- Medicine
- ……

Deep studies of thermal science:

Heat penetrates every substance of the universe, its rays occupy all parts of space. The theory of heat will hereafter form **one of the most important branches of general physics**.

— **Joseph Fourier**

Conclusions

Be practical as well as generous in your ideals. Keep your eyes on the stars, but remember to keep your feet on the ground.

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New challenges in multi-disciplines

- Power device
- Battery
- Medicine
- ……

Deep studies of thermal science:

Application

Conclusions

Try to do something:

Simple and effective (the development of measurement)

Try to do something：

Original、Useful、Surprising(Scientific genius)

Try to do something:

Typical and everlastingly new (Fourier law)

Application (make this world a better place)

Acknowledgment

- This work was supported by the National Natural Science Foundation of China (Grant Nos. 51827807 and 52130602).

Thank you for your attention!