Introduction to Nanotechnology and Nanoscience – Class#25

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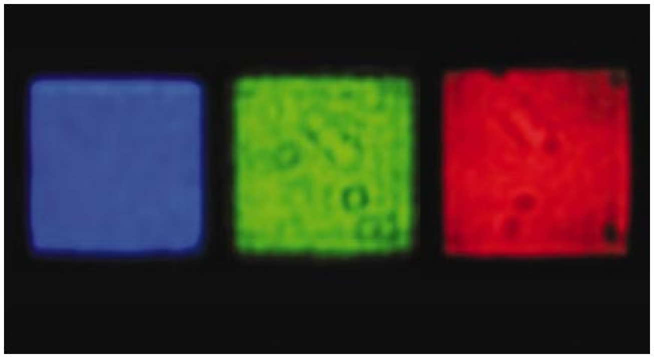
Outline

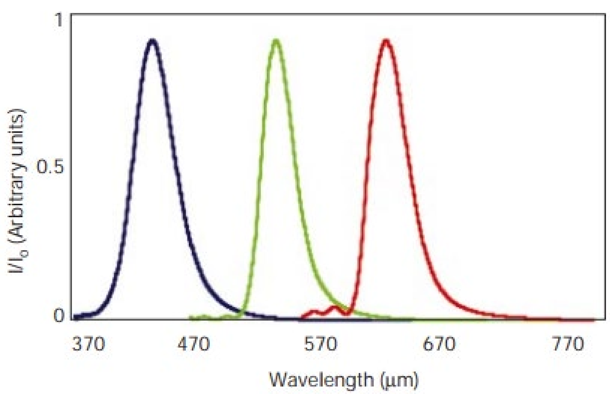
- Paper 11 –more presentation
- Recap
- Review for Quiz II
- Graphene

Enhanced transmission through array holes

- Transmission is stronger than diffraction theory predicted result
- Light energy on metal parts can also be transmitted through surface plasmon
- Acts like an optimal antenna, can control the dominate wave length using the size of the array holes

- Principle is to enhance the evanescent waves created in diffracting process of the array
- Tunneling effect, enhanced light transmission
- If the layer is thin the two surface waves can overlap and entangle



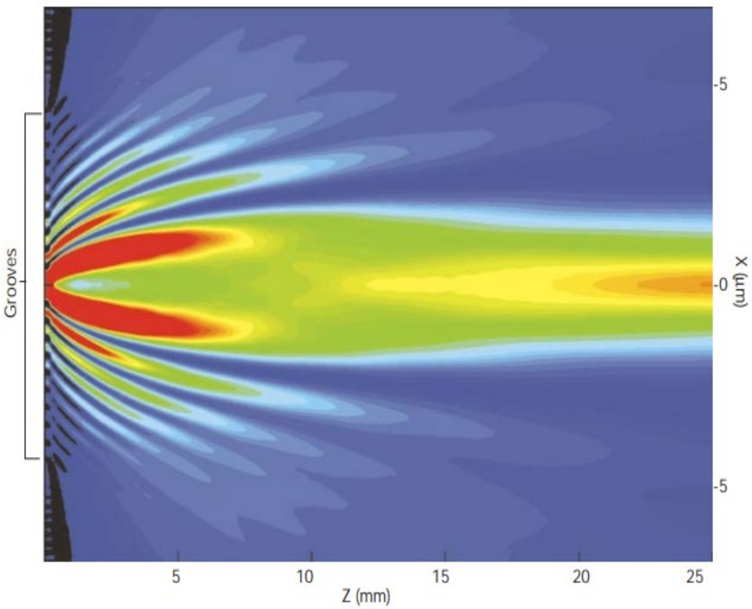


subwavelength hole light transmission

“the periods were 300, 450 and 550 nm, respectively, the hole diameters were 155, 180 and 225 nm and the peak transmission wavelengths 436, 538 and 627 nm.”

$$\lambda_{max}\sqrt{i^2+j^2} \simeq a_0 \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m+\varepsilon_d}}$$

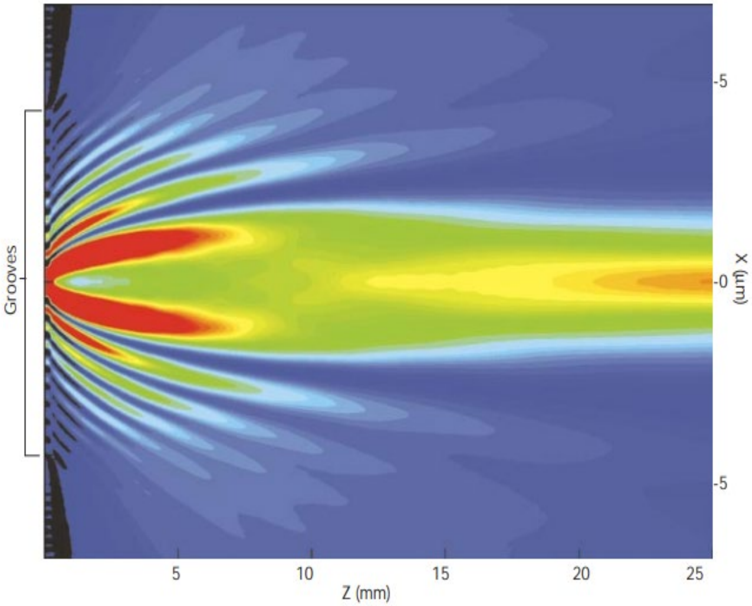
Single apertures



- In the previous experiment it was array of holes, in one aperture with period pattern beamed
- originally it should be diffracting effect showing light strips, the period pattern (output side) enhanced the middle stripe
- Light comes out from a small area

- Application:
  - high-density magnetooptic data storage
  - High quality light source
  - …

tpropagating mode and tunneling



- When the aperture is smaller than λ/2 on all side only tunneling
- Some direction is bigger than λ/2 propagating is introduced
- Use different pattern and shape to control both effects
- Some cases one mode is dominate

Potentials, applications and future studies

- Light generation. In organic LEDs, surface plasmon effect draws a lot of energy which could have been turned into light.
- add certain (periodic) pattern to control the sp process

- in solar cells use sp effect to enhance light absorption
- quantum cascade lasers

- Non-linear effects in SP studies (switches for SP based photonics)

- “new class of subwavelength photonic devices”
- waveguides, reflectors, beam splitters, enhanced transmission and beaming

Nanoplasmonics applications.

Johnson Chang / ME218

Introduction to Nanoplasmonics

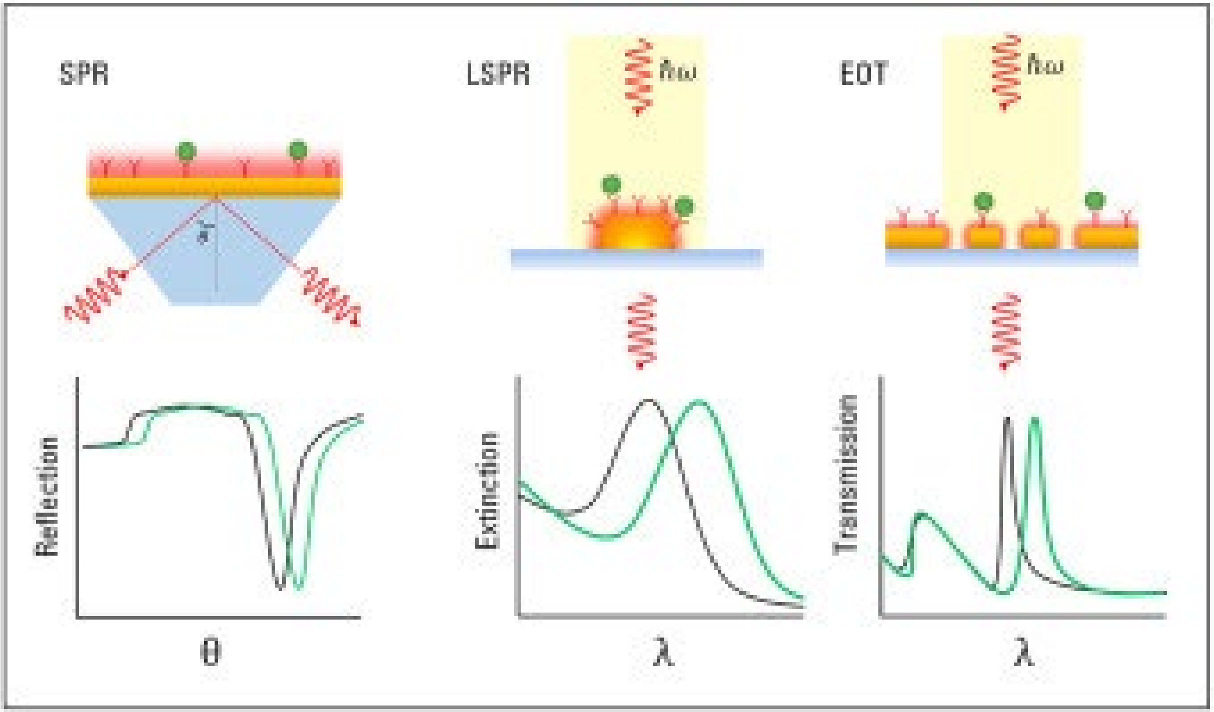
- **Definition:** Nanoplasmonics is the study of optical phenomena in the nanoscale vicinity of metal surfaces
- Unique optical properties of metallic nanostructures due to localized surface plasmon resonance (LSPR)

Fig1. Nanoplasmonics - Lycurgus Cup

Application - Nanoplasmonics for Biosensing

- Based on paper "Plasmonic Nanobiosensor for Ultrasensitive Detection of Protein Biomarkers" (Nature Nanotechnology, 2021)
- Developed a plasmonic nanobiosensor using gold nanoparticles for detecting extremely low concentrations of protein biomarkers
- Achieved detection limits down to attomolar (10^-18 M) concentrations
- Potential applications in early disease diagnosis

Nanoplasmonics for Biosensing



https://www.sciencedirect.com/science/article/abs/pii/S0003267021006681

Fig2. the theory of Nanoplasmonic biosensing for popular detection schemes - SPR, LSPR, and EOT

Application - Nanoplasmonics for Optical Trapping and Manipulation

- Based on paper: "Optical Manipulation of Nanoparticles Using Plasmonic Nanoantennas" (Science, 2022)
- Demonstrated the use of plasmonic nanoantennas to optically trap and manipulate individual nanoparticles
- Enabled precise control and positioning of nanoparticles for applications in nanomanufacturing and single-molecule studies

Nanoplasmonics for Optical Trapping and Manipulation

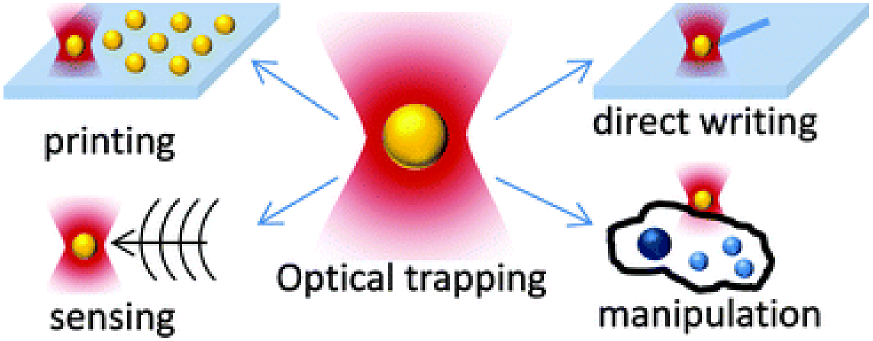
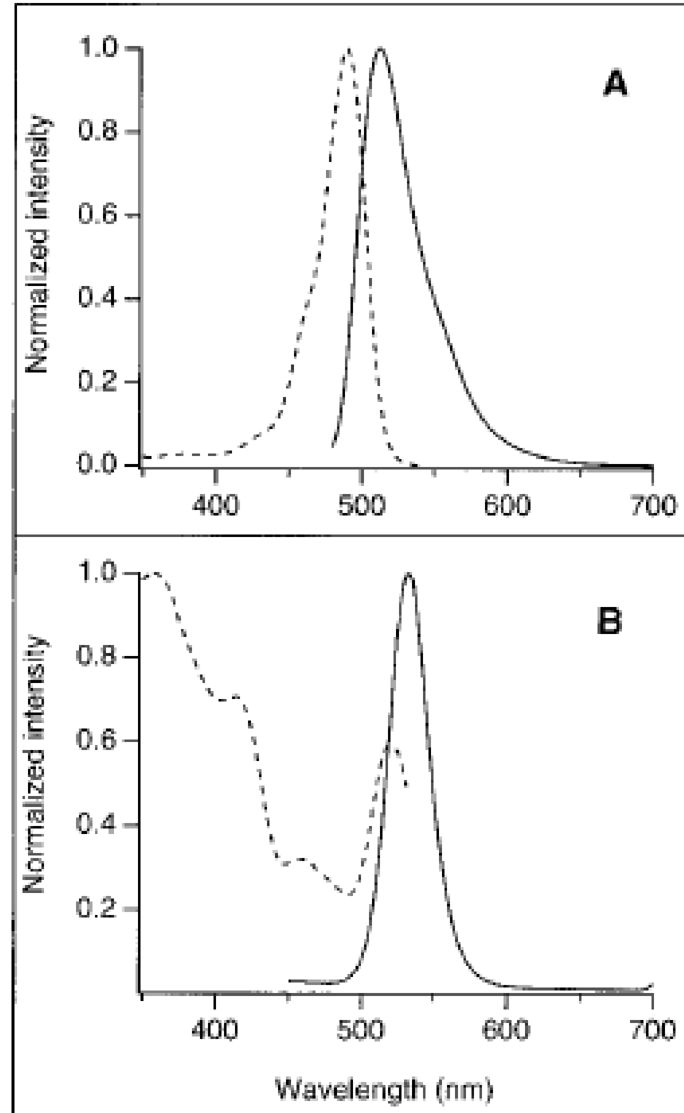


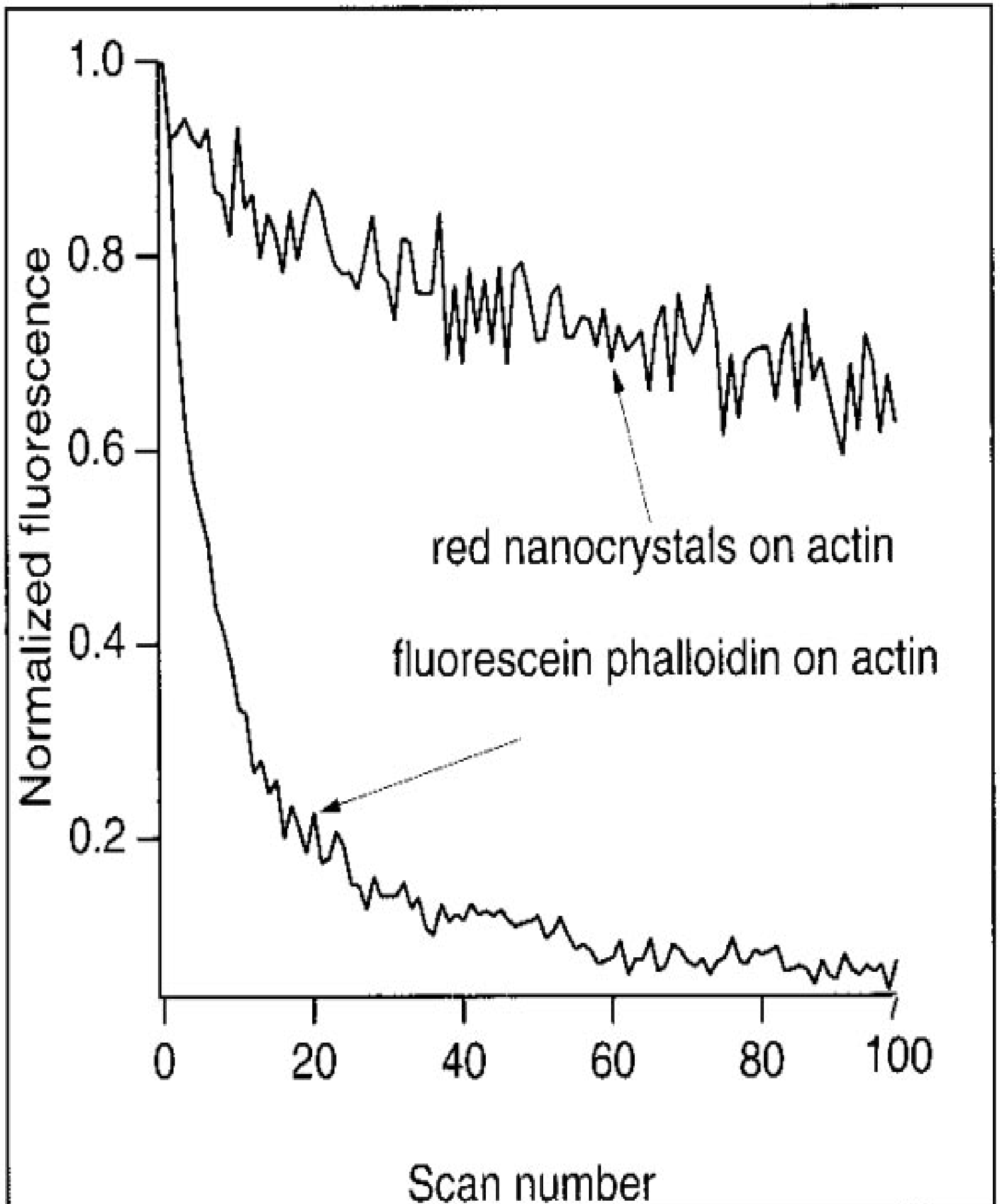
Fig3. Optical trapping and manipulation of plasmonic nanoparticles, an area of current interest with potential applications in nanofabrication, sensing, analytics, biology and medicine.

https://pubs.rsc.org/en/content/articlelanding/2014/nr/c3nr06617g

Semiconductor Nanocrytals

- Adjusting size and composition gives emission range of 400nm to 2μm
- Narrow, symmetric spectrum
- Many different colors can be excited with a single wavelength



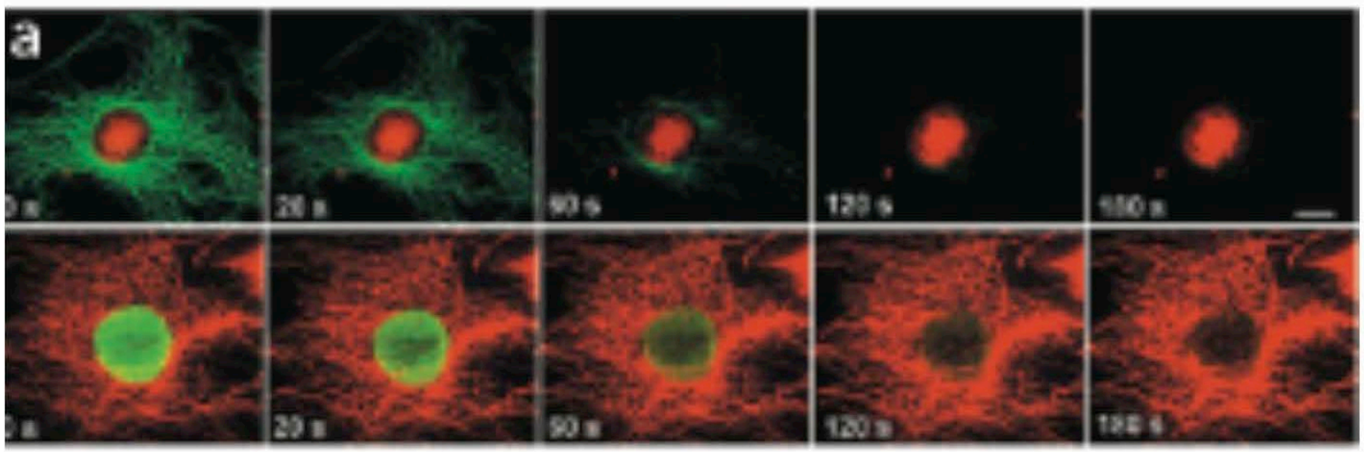


- Intensity of fluorescence fades at a much slow rate than traditional organic molecules used for staining (phalloidin in this case)

- Nanocrystal probes may prove useful for:
  - x-ray fluorescence
  - x-ray absorption
  - electron microscopy
  - scintillation proximity imaging

Additional Properties of Qdots

- High quantum yield
- Very stable



Alivisatos, Nature Biotech., 2004

Metallic Nanoparticles

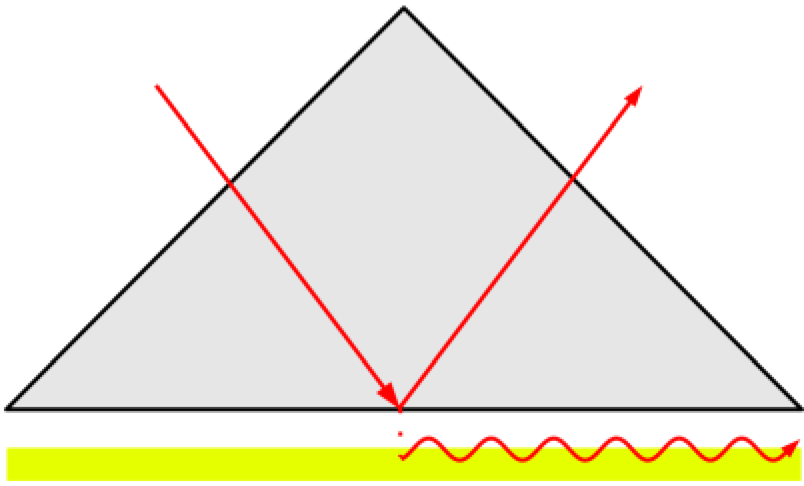
- Consists noble metal nanocrystals that have valence electrons (electrons which are present at the outer most shell of the atom) excited by incident light via plasmon excitation
- Excitation of valence electrons of gold nanocrystals causes a great increase in the cross section for absorption or emission of EM radiation from any molecule
- The change in cross section changes the plasmon resonance so it is possible for a wide range of wavelengths for detection

Surface Plasmon Resonance

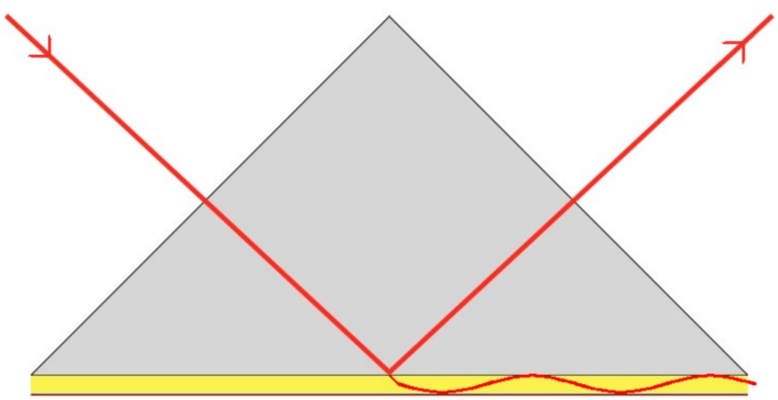
- Basis of many standard tools for measuring adsorption of material onto planar metal or metal nanoparticles
- Surface electromagnetic waves that propagate parallel along a metal/dielectric (or metal/vacuum) interface. Since the wave is on the boundary of the metal and the external medium, these oscillations are very sensitive to any change of this boundary, such as the adsorption of molecules to the metal surface
- Typical metals that support surface plasmons are **silver** and **gold**, but metals such as copper, titanium, or chromium can also work

Two Basic Configurations

- Otto setup, the light is shone on the wall of a glass block, typically a prism, and totally reflected. A thin metal (for example gold) film is positioned close enough, that the evanescent waves can interact with the plasma waves on the surface and excite the plasmons



- Kretschmann configuration, the metal film is evaporated onto the glass block. The light is again illuminating from the glass, and an evanescent wave penetrates through the metal film. The plasmons are excited at the outer side of the film. This configuration is used in most practical applications



University of California at Berkeley
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Mechanical Engineering Department

ME118, Spring 2017 **Liwei Lin**

Quiz II (80 minutes)

Close book, close notes, open two pages formula sheet

Please answer questions as concise as possible

Problem 1, Concepts (60 points)

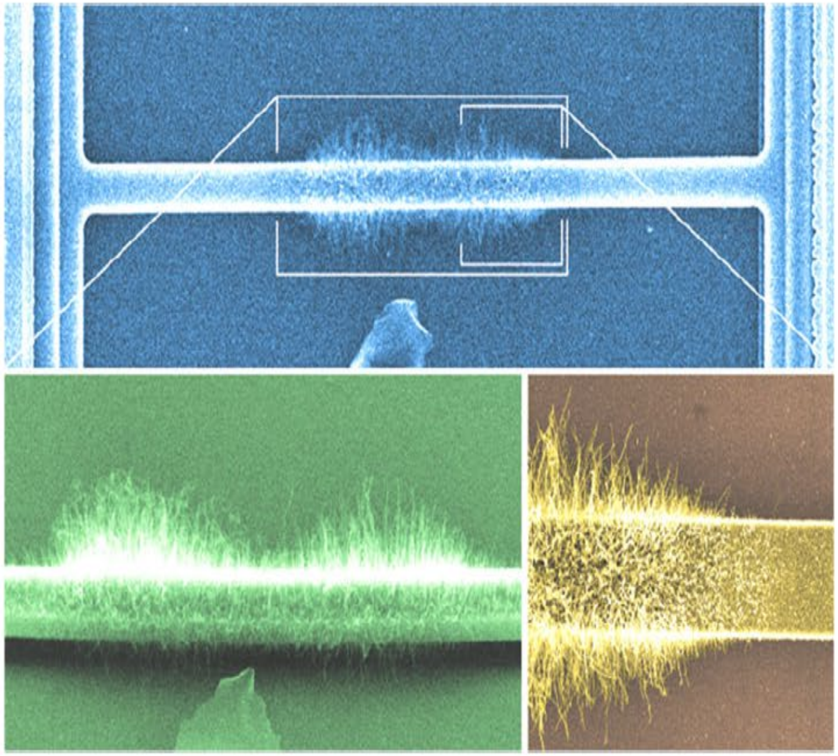
Please answer the questions as concise as possible (less than 50 words). Please use illustrations if they may help your answers

a. Draw a schematic diagram of a nanowire-based MOSFET where the nanowire is used as the "channel", including the process flow to make this MOSFET. (10%)

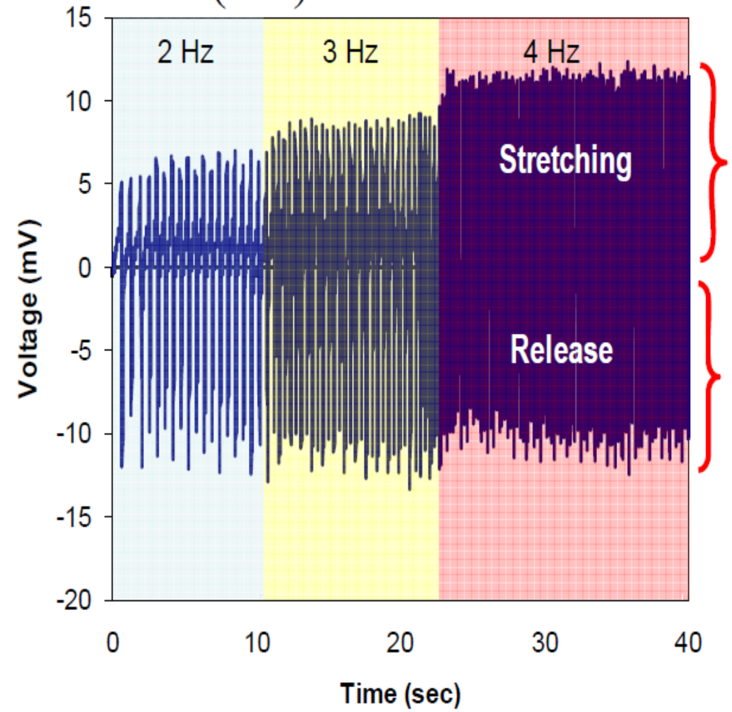
b. List at least 6 differences between the conventional electrospinning and the dip-pen based near-field electrospinning process (6%)

c. What is the “apparent” or “measured” radius (width) **ρ** of a nanowire of radius **r** if the diameter of the AFM tip is **R**? Derive an algebraic expression for **ρ**, showing all relevant steps (6%).

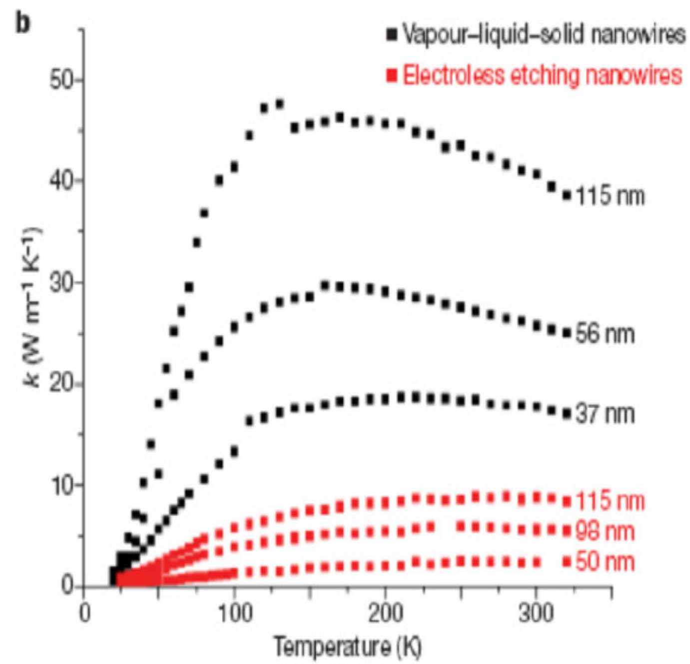
d. Explain the key mechanisms/methodologies/conditions to grow silicon nanowires as shown in the figure? What is the key reason that the nanowires only grow in the central regions of the suspended structure? Why is the nanowire length at the center of the heater is shorter than the regions slightly off the center (8%)



e. The figure shows the testing results in the PVDF nanofiber-based nanogenerator paper. What is the reason that the nanogenerator can generate electricity and why does the positive output voltage increase as the applied frequency increases? Why does the negative output voltage seem to be the same as the applied frequency increases? (8%)



f. In the discussion of the thermoelectric figure of merit, we showed an interesting result from silicon nanowires in the figure. Which type of nanowires has higher figure of merit and why? What is the fundamental reason that these two types of silicon nanowires have different thermal responses as shown? (6%)



g. Please explain the different mechanisms in creating the optical emission outputs of (1) quantum dots, (2) metallic nanoparticles, and (3) photonic crystals? (6%)

h. What is the major problem in MOSFET that "FinFET" is trying to address? Please draw a FinFET, define all regions, and explain the "gate length" and "gate width"? Please draw a figure showing the other major competing technology to FinFET? (10%)

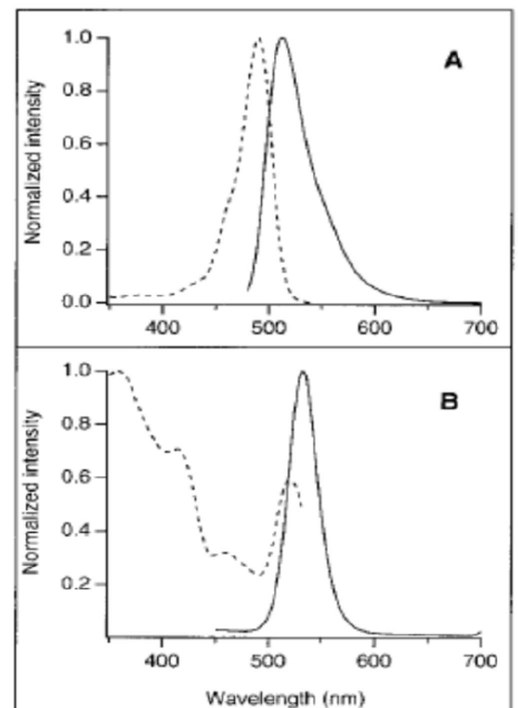
a) You are given a series of quantum dot solutions:

Blue **Green** **Yellow** **Red**

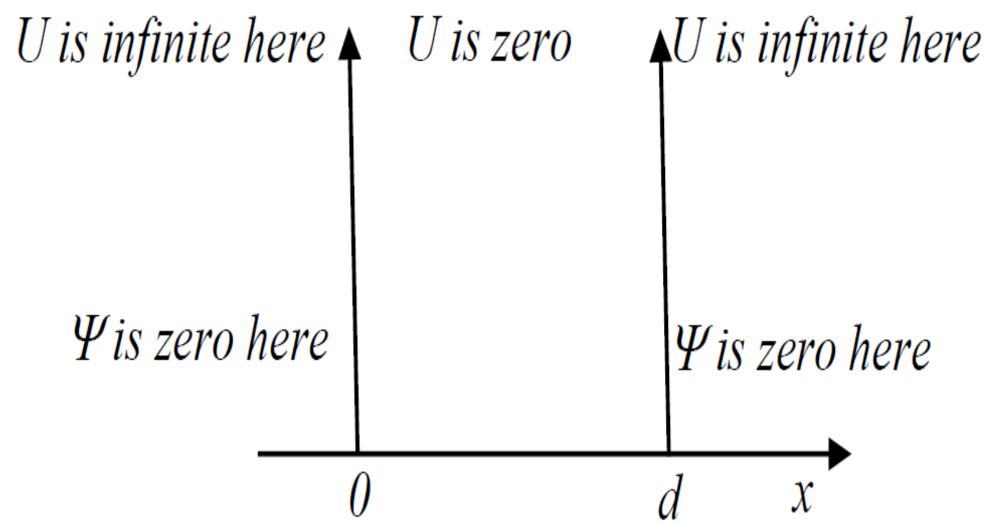
Use an arrow to indicate quantum dot size from small to large. (5%)

b) How does the bandgap change with respect to the size of the quantum dot? (5%)

c) The figure shows the adsorption (dashed line) and emission spectrum (solid line) of: (A) conventional fluorophores, and (B) quantum dots. Please describe at least two key differences in the figures and why quantum dots are better in real applications (10%)



is the system energy. You are asked to solve the wave functions and eigen energies for the infinite square potential shown. The solutions are of the form *Asin(kx)*, so the wave function is zero at $x=0$ boundary. (a) State the condition at $x=d$ and state the allowed values of k. (b) Write down an equation for the Eigen energies. (c) Sketch the third state at t=0 on the figure below.



Synthesis and Applications of Graphene in MEMS-based Systems

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Outline

- Graphene synthesis by local CVD
  - Overview, synthesis methods, local CVD …

→What are the special characteristics?

→Does it work?

→Can it improve the graphene production?

- Flexible gas sensors based on graphene FETs
  - Flexible substrate, graphene FETs, sensing characterizations …
- Graphene-on-diamond thin film UV detector
  - Concept, fabrication, sensor testing results …

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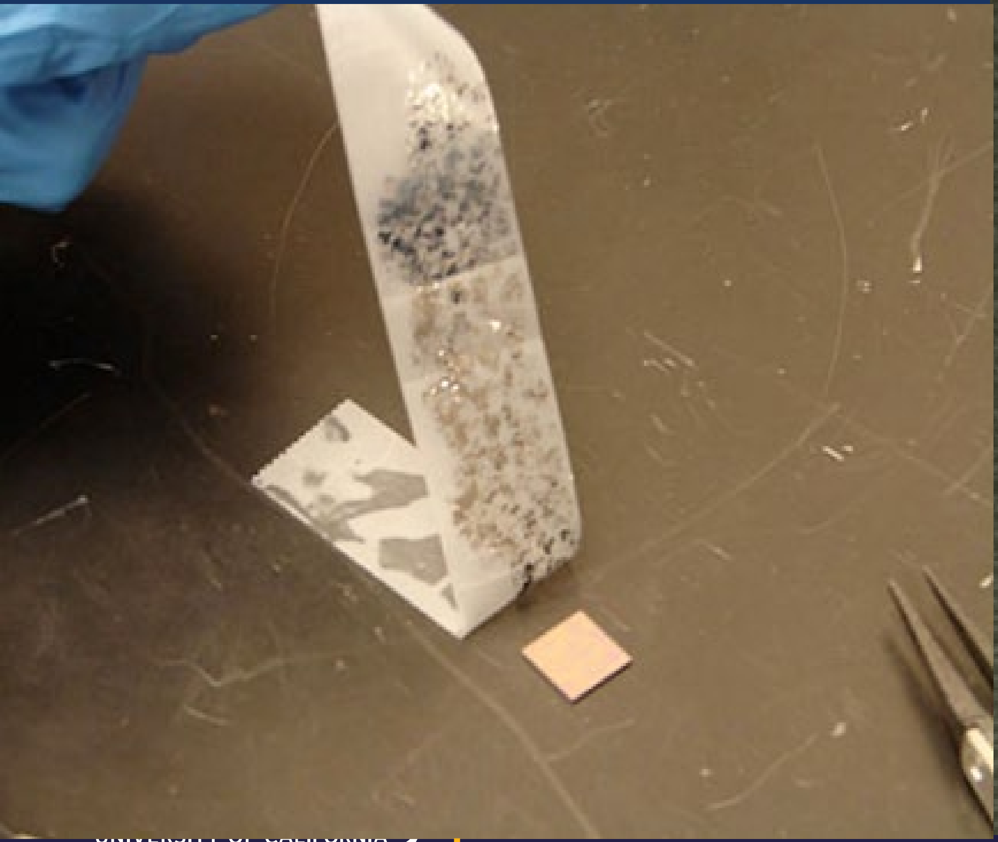
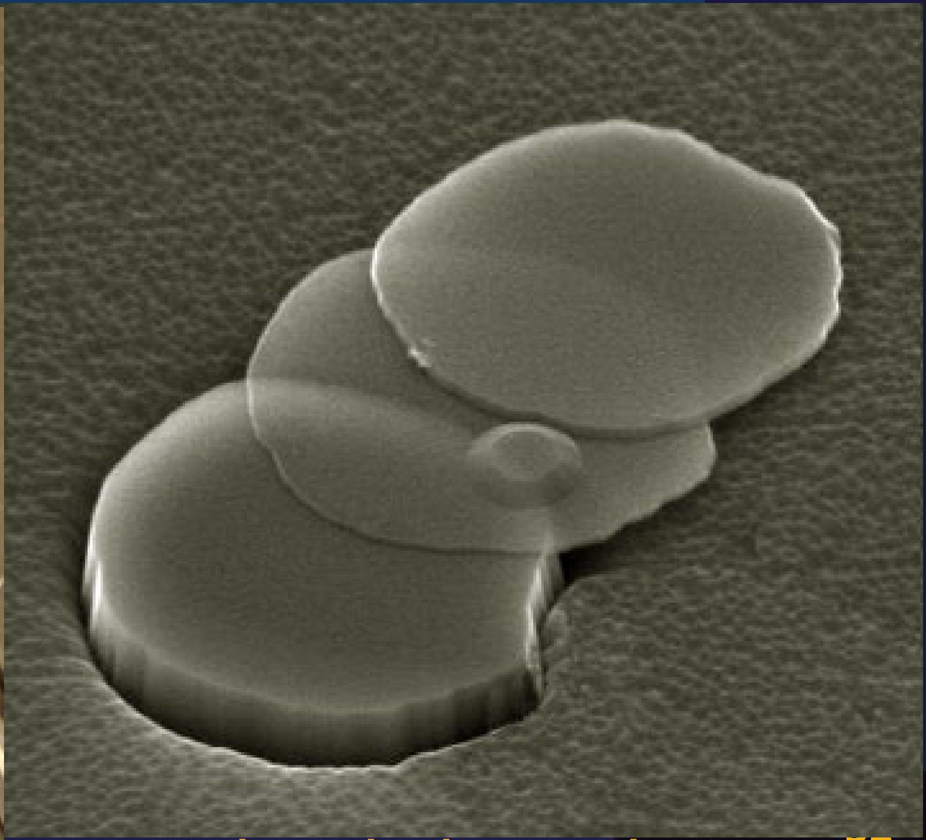
How to Synthesize Graphene?

- The **earliest** and also the most widely used method to acquire **high quality graphene** is mechanical/chemical exfoliation of bulk graphite



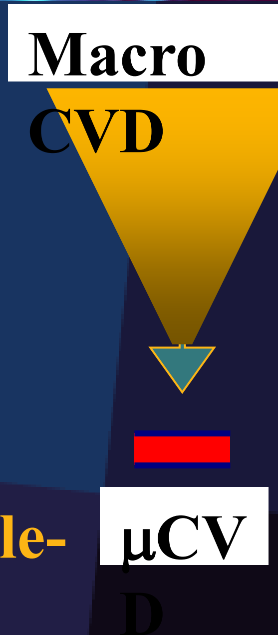
www.sciam.com



www.condmat.physics.manchester.ac.uk

MEMS for High Cooling Rate?

- **Several minutes to several hours** for a common CVD system to cool down
- By abruptly exposing CVD chamber to outside environment or by flowing cold gas into the chamber at a high rate, time constant can be reduced to **~10 seconds**
- It is difficult to further reduce thermal time constant because of **large heat capacity**
- Large heat capacity can be brought down significantly by shrinking down the size of the CVD system → **micro CVD**



Qin Zhou and Liwei Lin, "Enhancing Mass Transport for Synthesizing Single-walled Carbon Nanotubes via Micro

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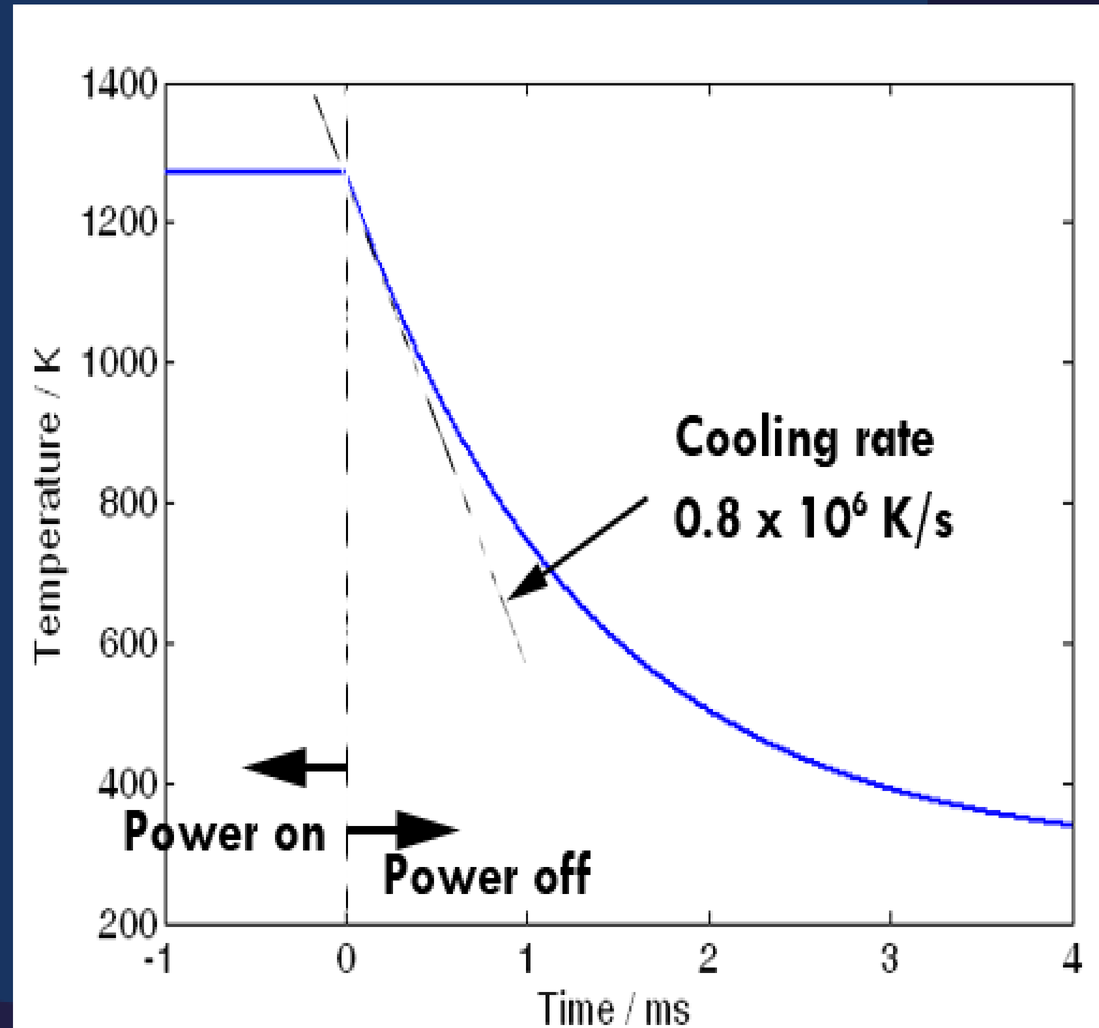
Cooling Rate in μCVD

- **The heat capacity C_h of the system scales with volume or L^3**
- **The heat resistance R_h, on the other hand, scales with L^{-1}**
- **the time constant of the system $\tau_h = R_h C_h$ should scale with L^2**
- **CVD system from macro (0.1~1m) down to micro (~ 300μm) ➔ ~10^{-6} reduction of time**



- **Time constant from ~ 10 mins down to ~ one millisecond!!**

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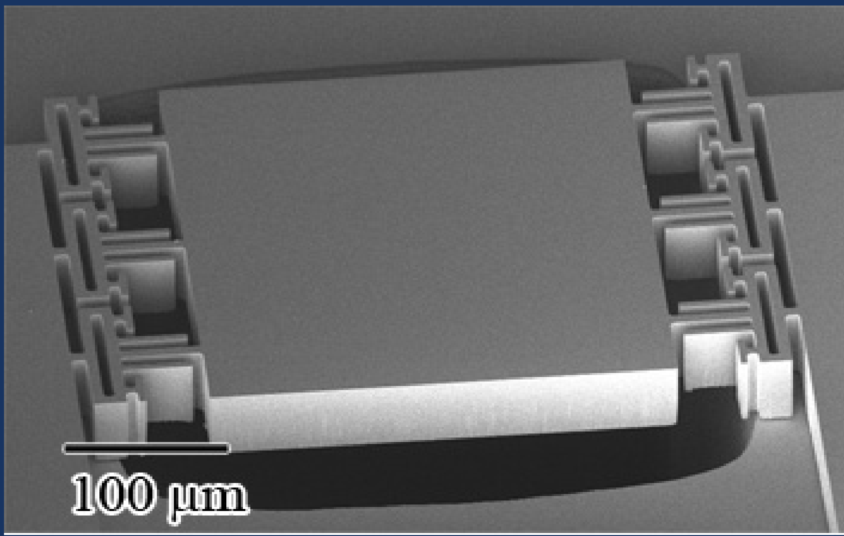
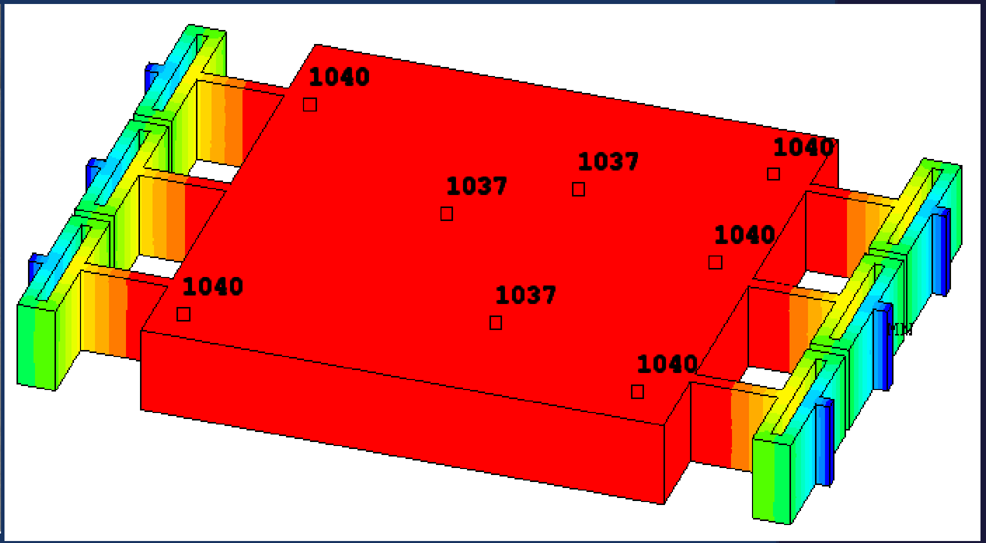
μ-CVD MEMS Structure Design





- Folded beams to release thermal strain on the platform
- ANSYS® analysis shows a heating stage at 1000ºC with temperature variations within 5ºC
- Uniform temperature field is critical for nickel to absorb carbon for consistent number of graphene layers

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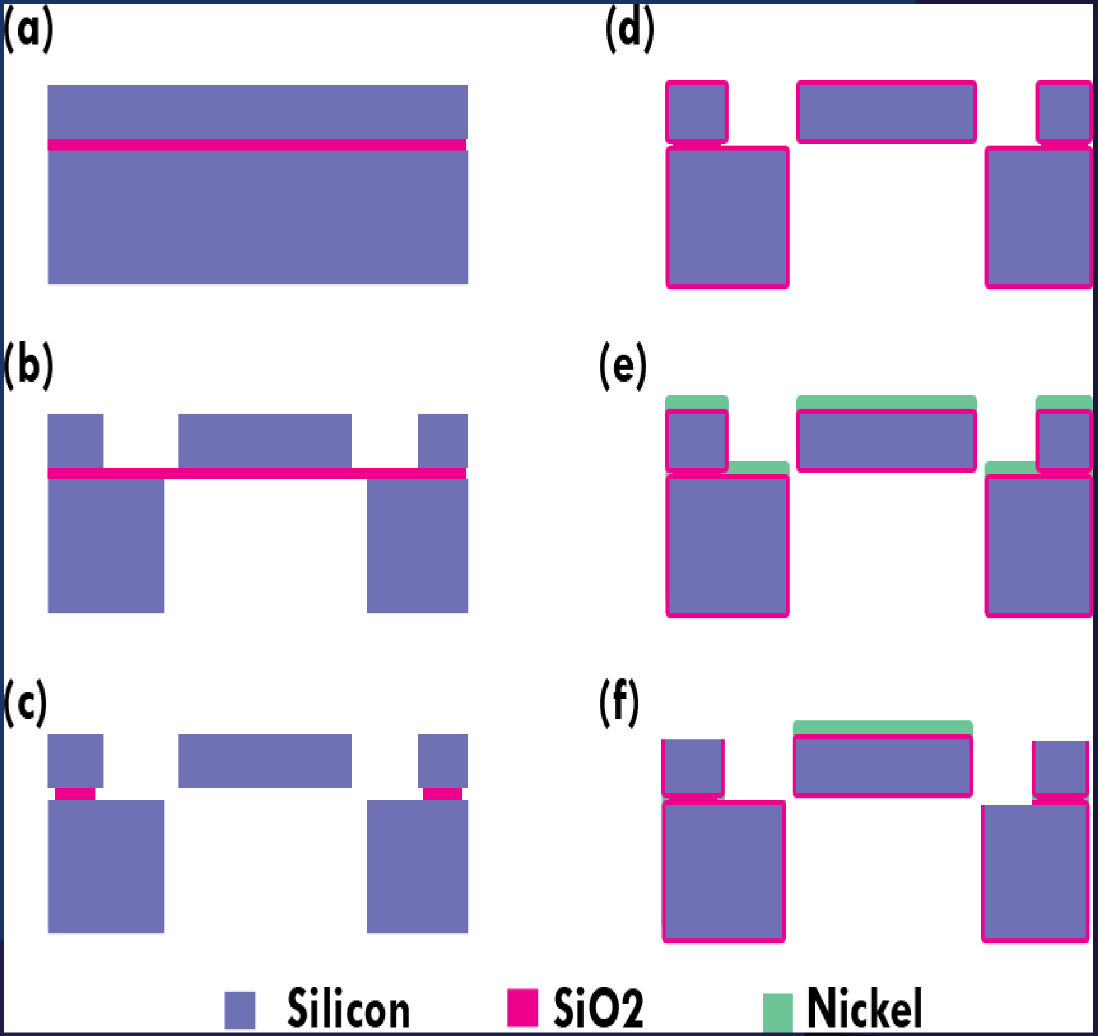
Device Fabrication

- (a) SOI wafer.
- (b) Back-side opening and front side etch for heating stage
- (c) Structure release in buffered HF solution.
- (d) Thermal oxidation to grow 150nm SiO2
- (e) Evaporate 300nm thick nickel layer.
- (f) Etch away nickel and SiO2 on anchors.



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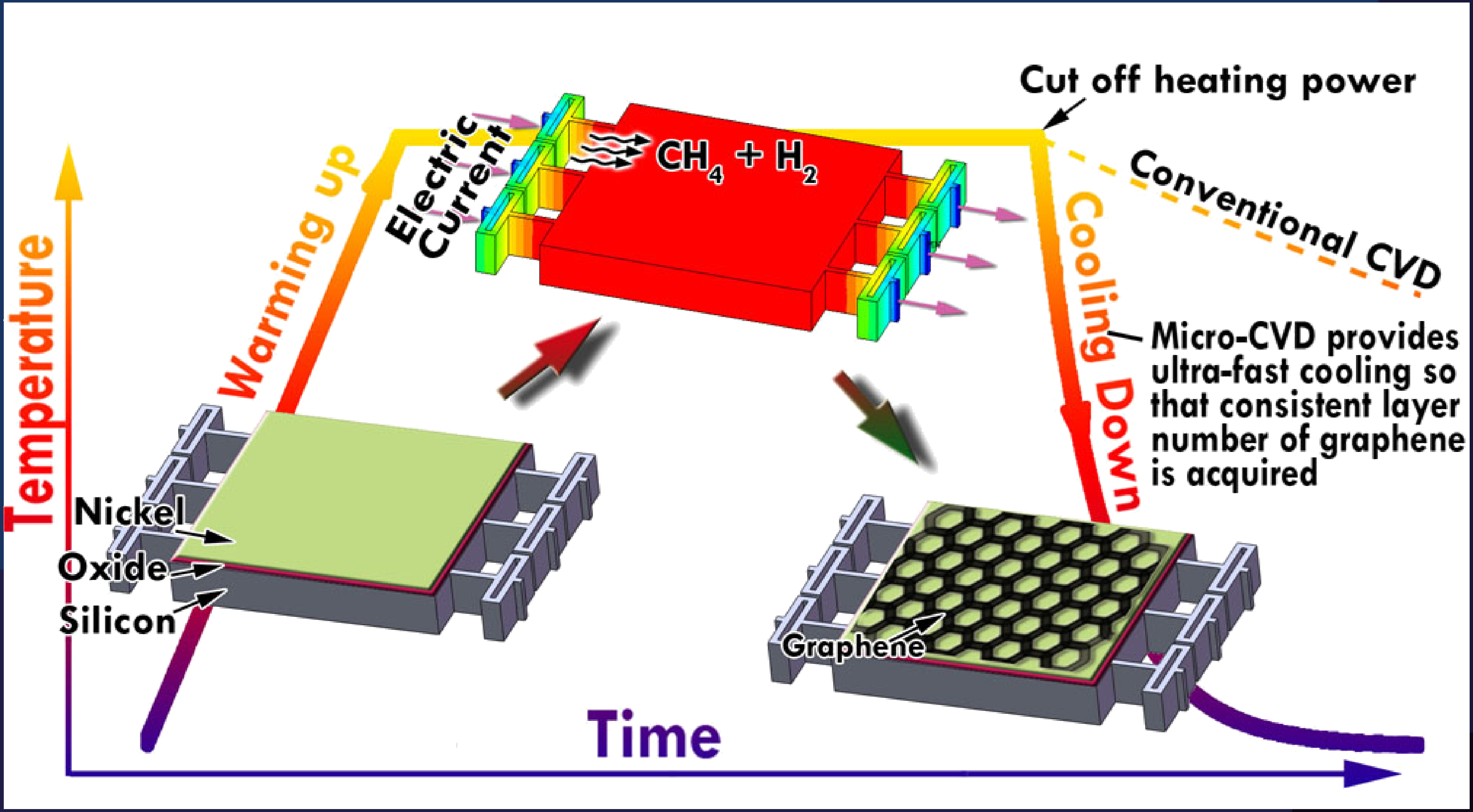
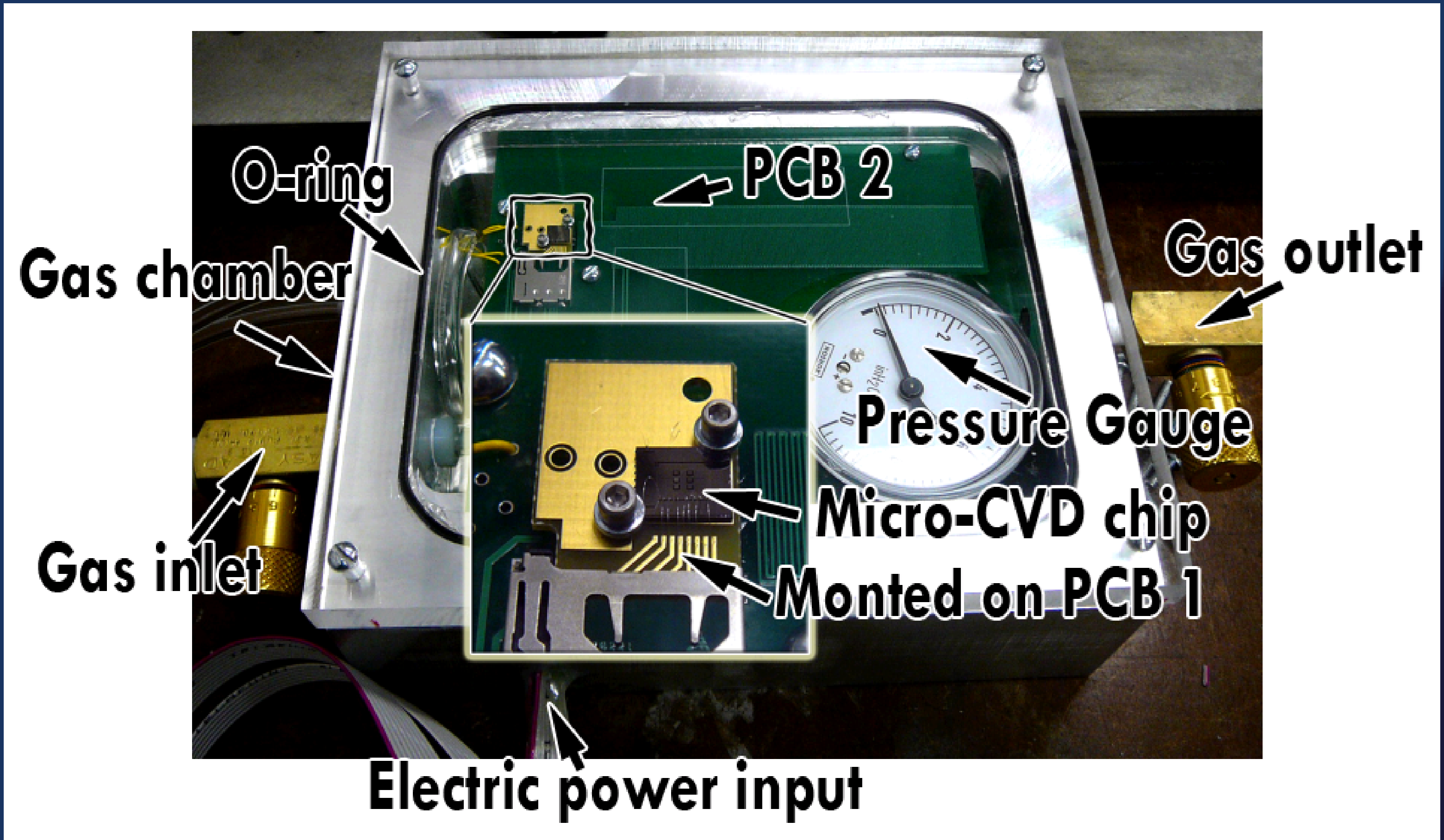
Graphene Synthesis by μ-CVD

- The μ-CVD system provides high cooling rate – corresponding to more **uniform layer**?



Experimental Setup



- μ-CVD chip is mounted on a printed circuit board for gas and electrical interface

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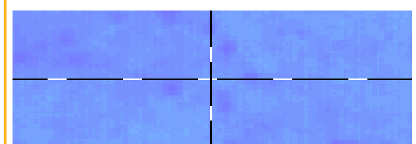
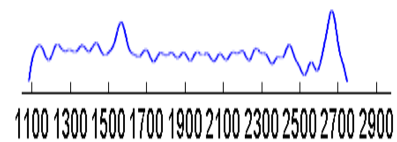
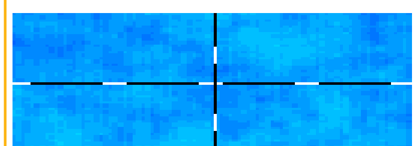
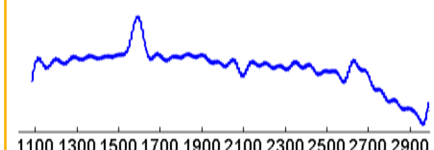
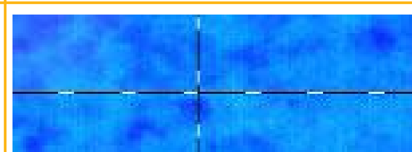
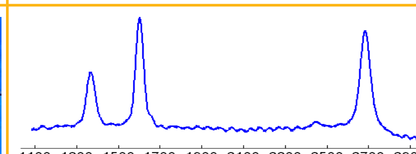
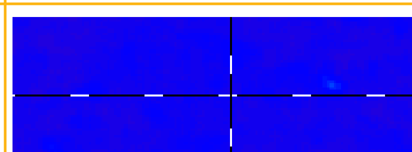
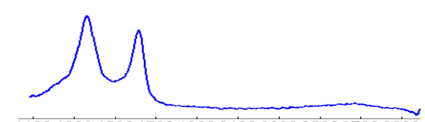
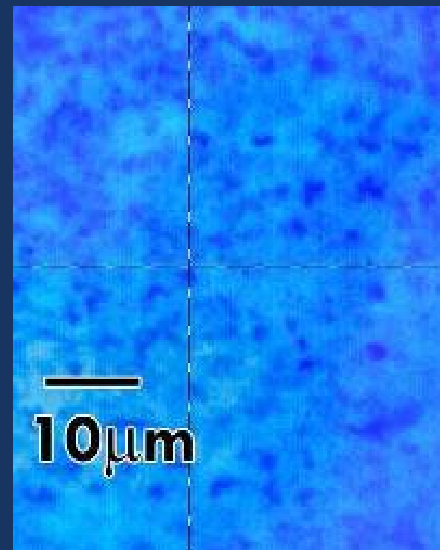
Experimental Results

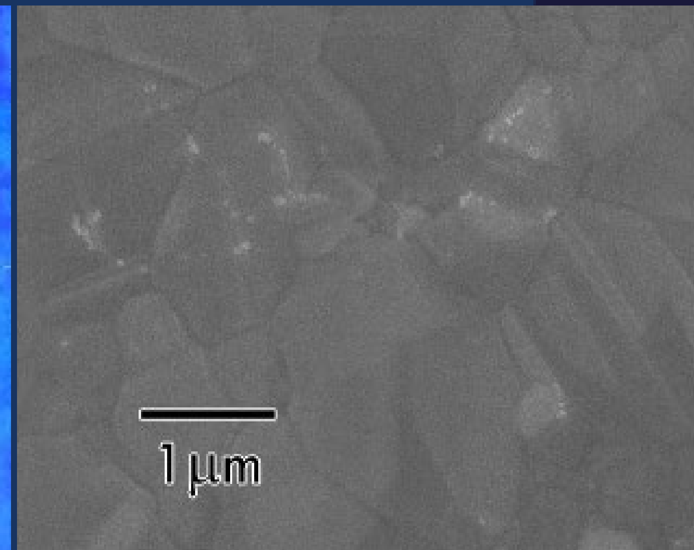
- Joule heating produced an estimated temperature of 1000 ºC in hydrogen environment. Methane is introduced as the carbon source for 5 mins

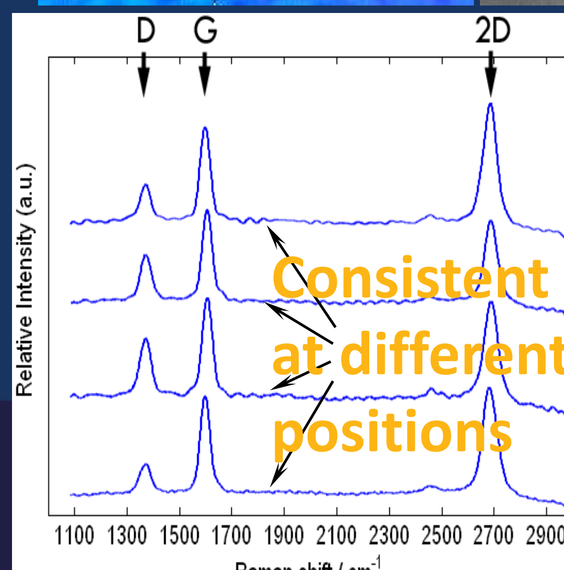
Power (mW)	Result	Optical Image	Raman Spectra	Success?
220	No material detected			No
250	dots could be seen			No
280	Scattered dots with darker color			Yes
310	Very dark			No
350	Supporting beams failed after few seconds heating			No

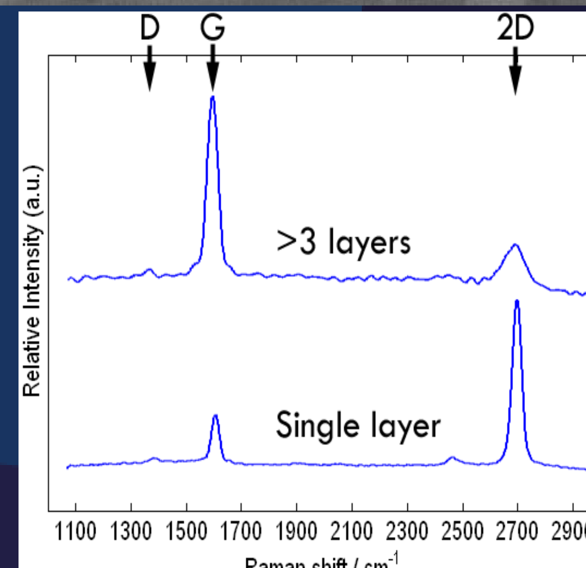
Results and Analyses

- The intensity ratio of G band and 2D band indicates **bilayer graphene** in an area of 90000μm^2 (300×300μm)
- Raman spectra of a **furnace grown graphene sample vary** measurement positions









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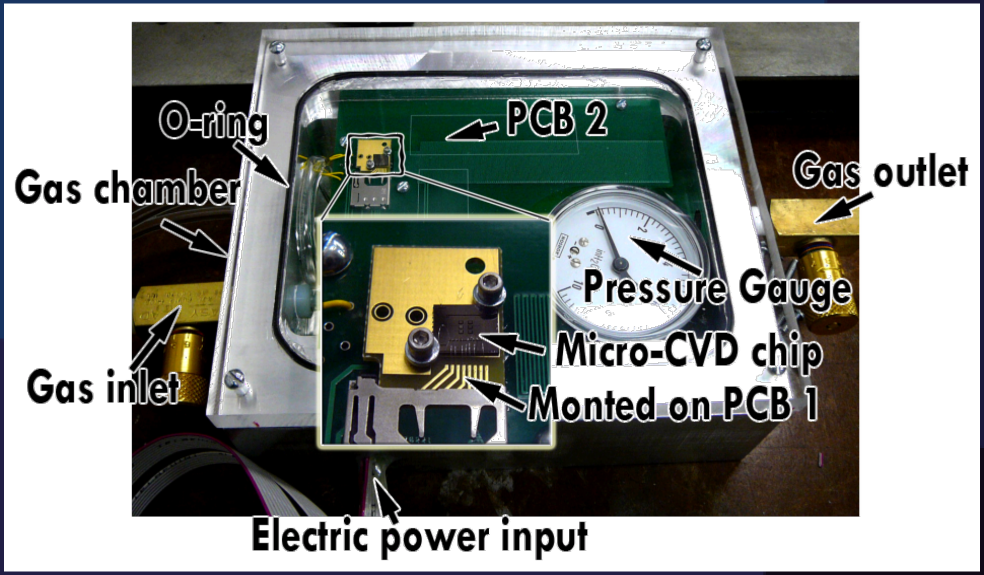
Short Summary

- Uniform bi-layer graphene synthesis in the miniaturized CVD platform of $300 \times 300 \mu m^2$ in size using nickel
- Small heat capacity of the Micro-CVD system results in a very short thermal time constant
- The lack of annealing step, however, creates more defects. This problem might be overcome by using an electrical control circuit to slightly reduce the cooling rate and post-annealing processes.



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Outline

- **Graphene synthesis by local CVD**
  - Overview, synthesis methods, local CVD …
- **Graphene synthesis by droplet CVD**
  - Continuous graphene sheet? Application example ...

→ ***Does it work?***

→ ***Can one make discontinuous metal droplets with continuous graphene sheets on top?***

→ ***Device demonstration?***

- **Graphene-on-diamond thin film UV detector**
  - Concept, fabrication, sensor testing results …

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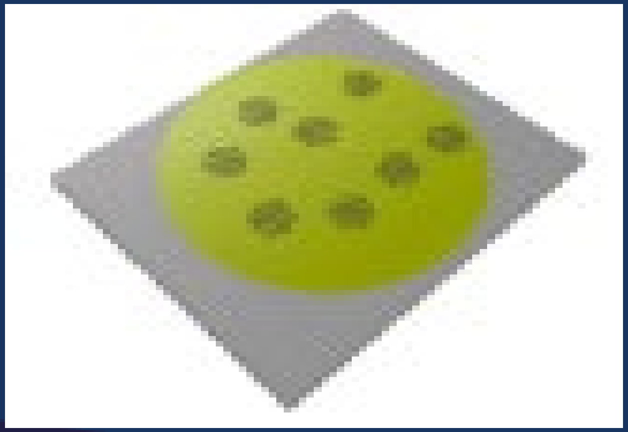
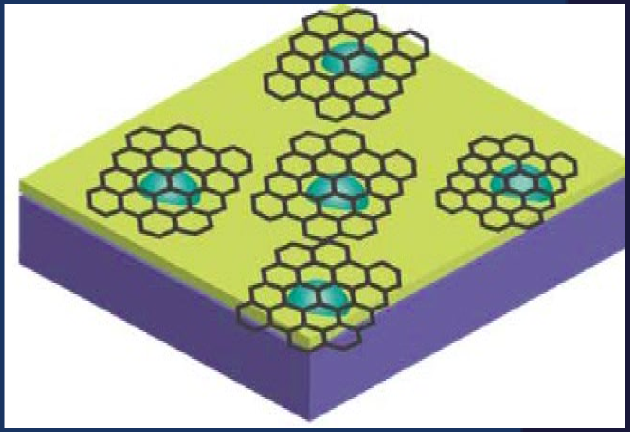
Multiple Droplets CVD?

- **Large area graphene via multiple droplets?**
- **Continuous graphene with discontinuous metal?**
- **Controllability and process parameters?**
- **Quality of graphene film?**
- **Nickel or copper as the catalyst material?**
- **Potential applications?**



Synthesis by a Single Droplet

?



Synthesis by Multiple Droplets

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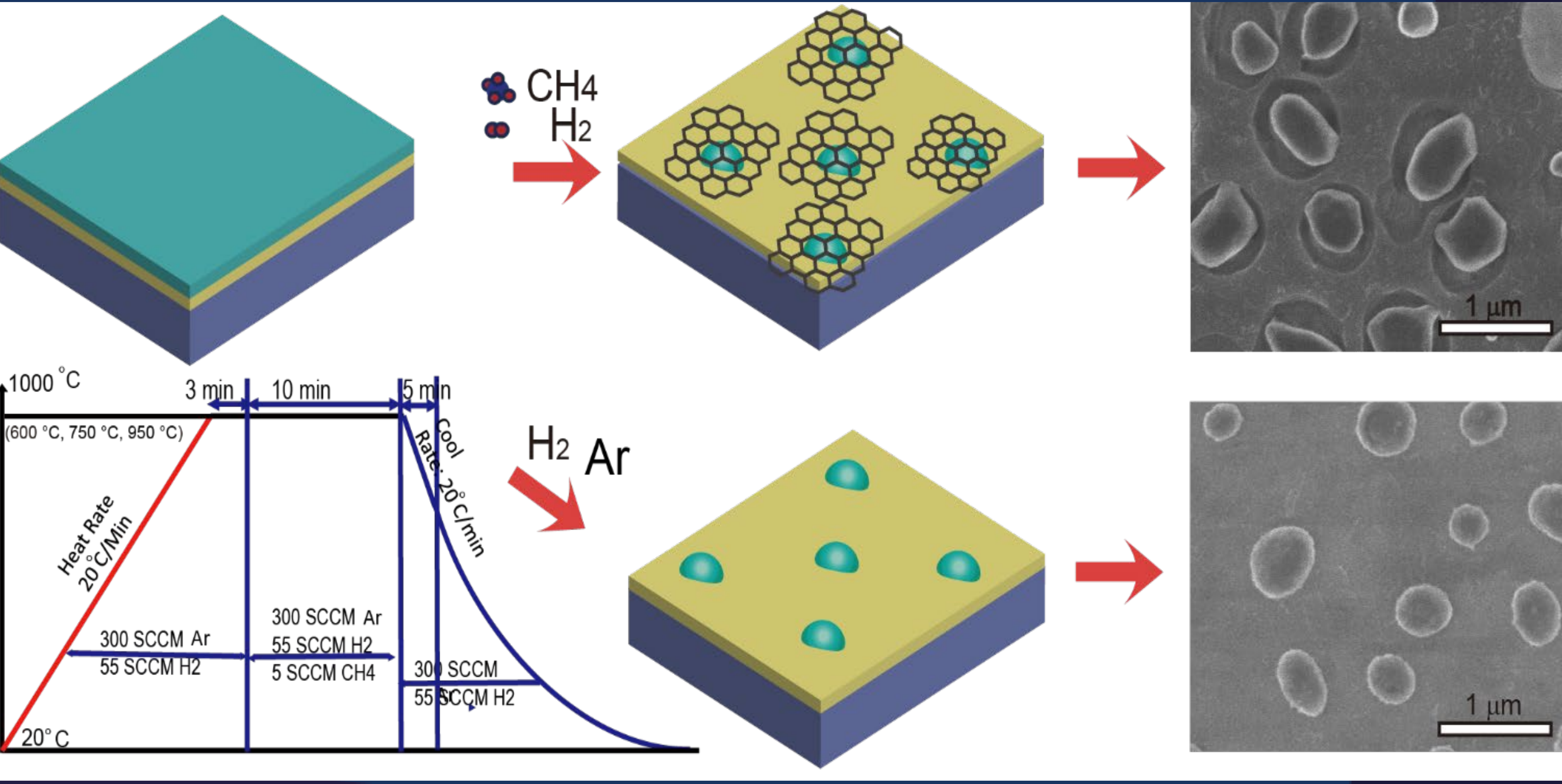
Large Area via Multiple Droplets?



Scattered graphene of hexagonal tents cover the metal droplets

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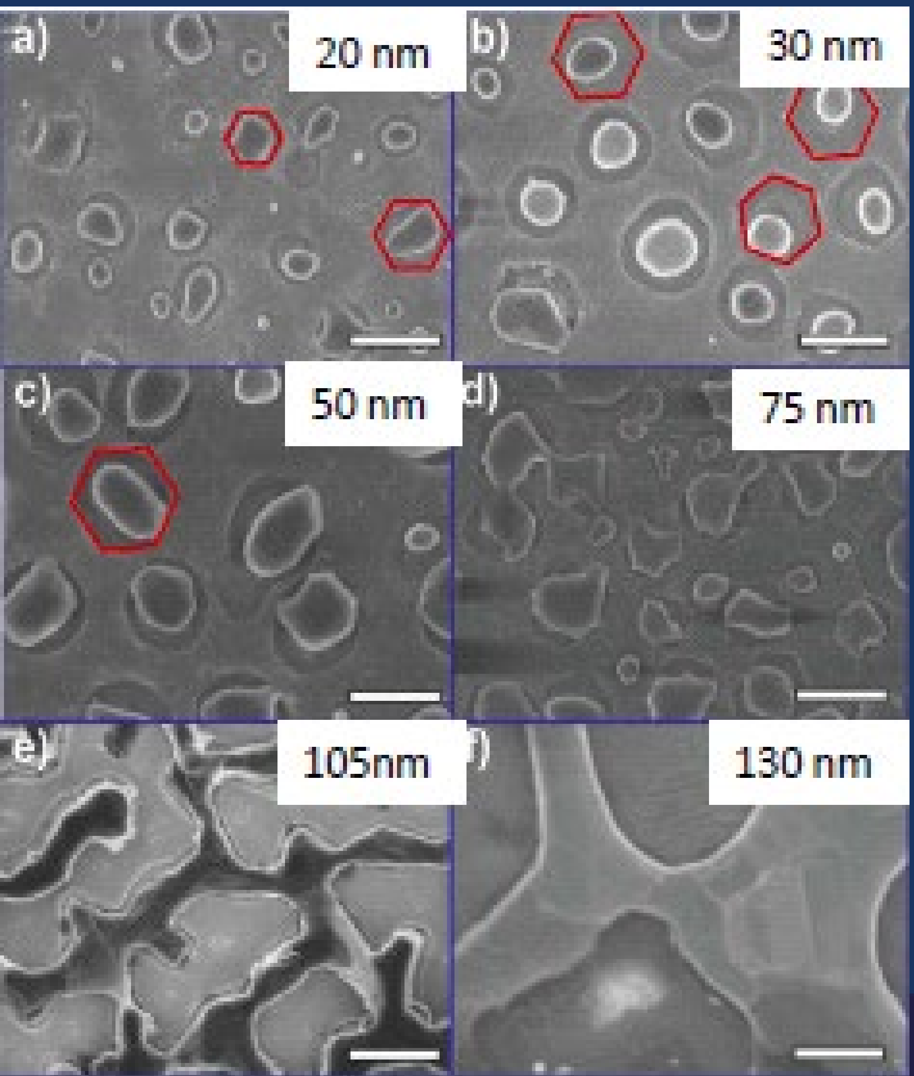
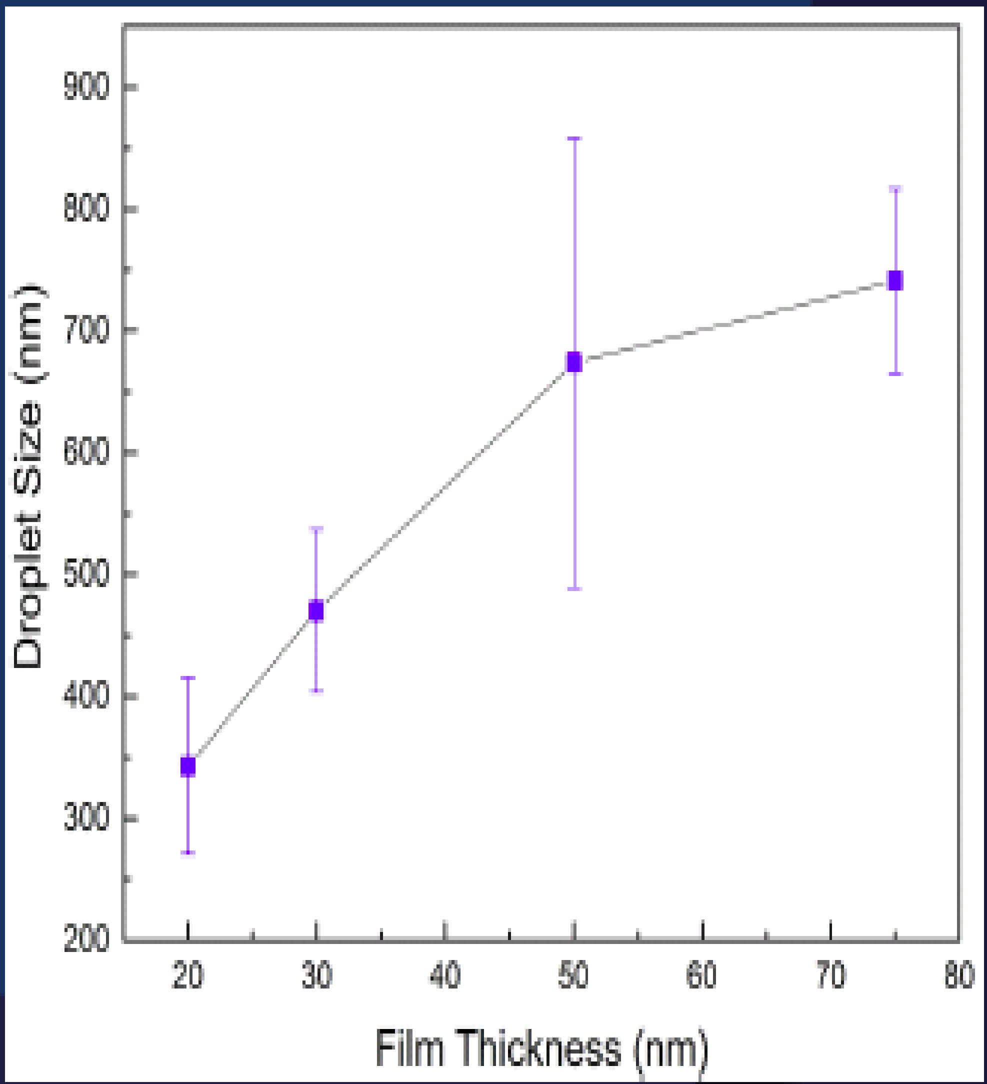
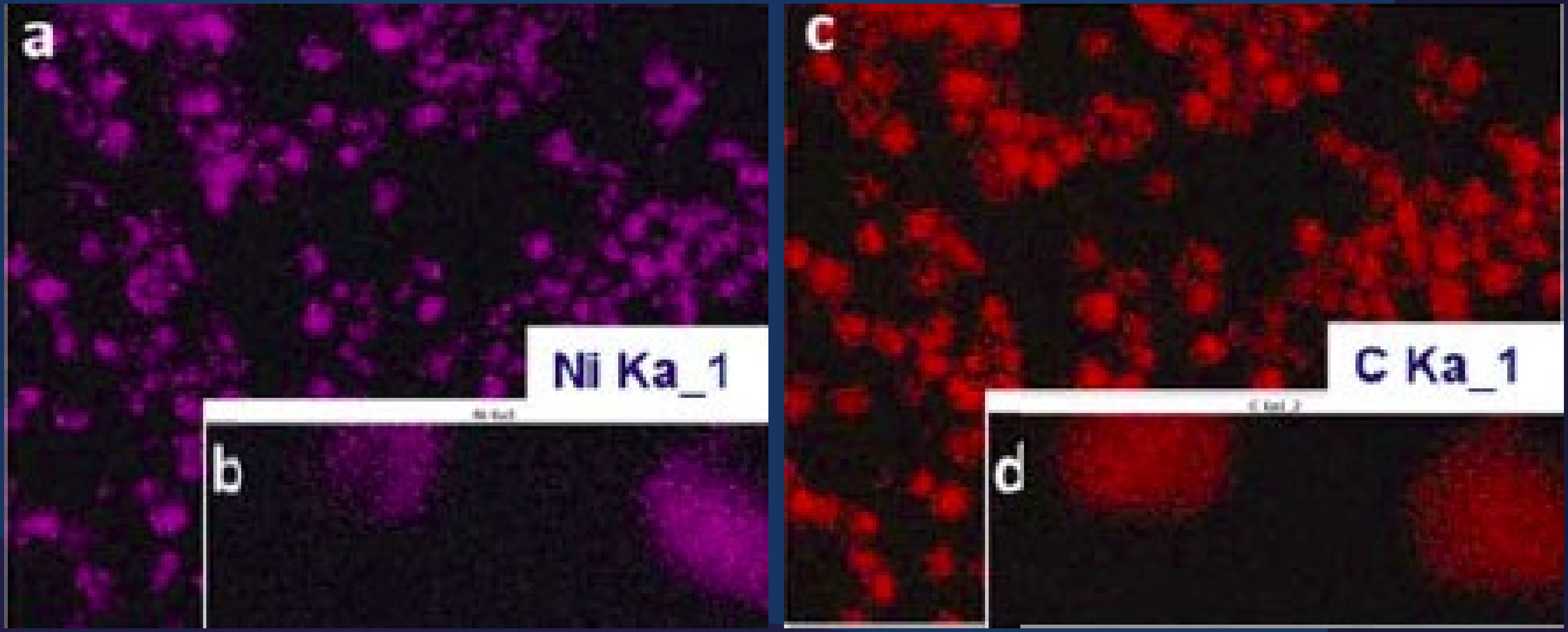
Ni Droplets Synthesis Results





EDS Spectrum for Ni & C Contents

- Slightly larger carbon contents at the same spots
- Possible outgrowth of graphene?



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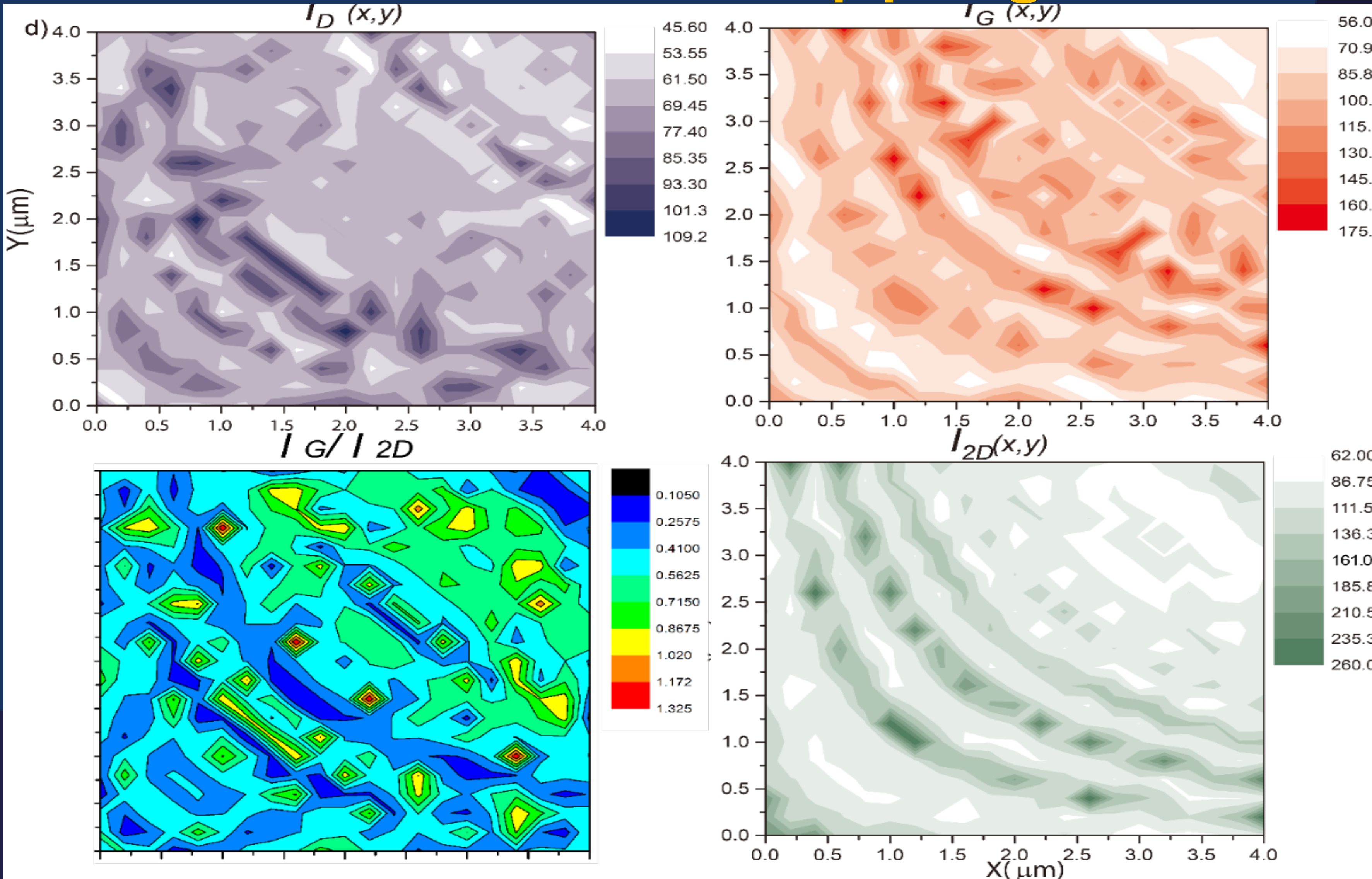
Raman Mapping

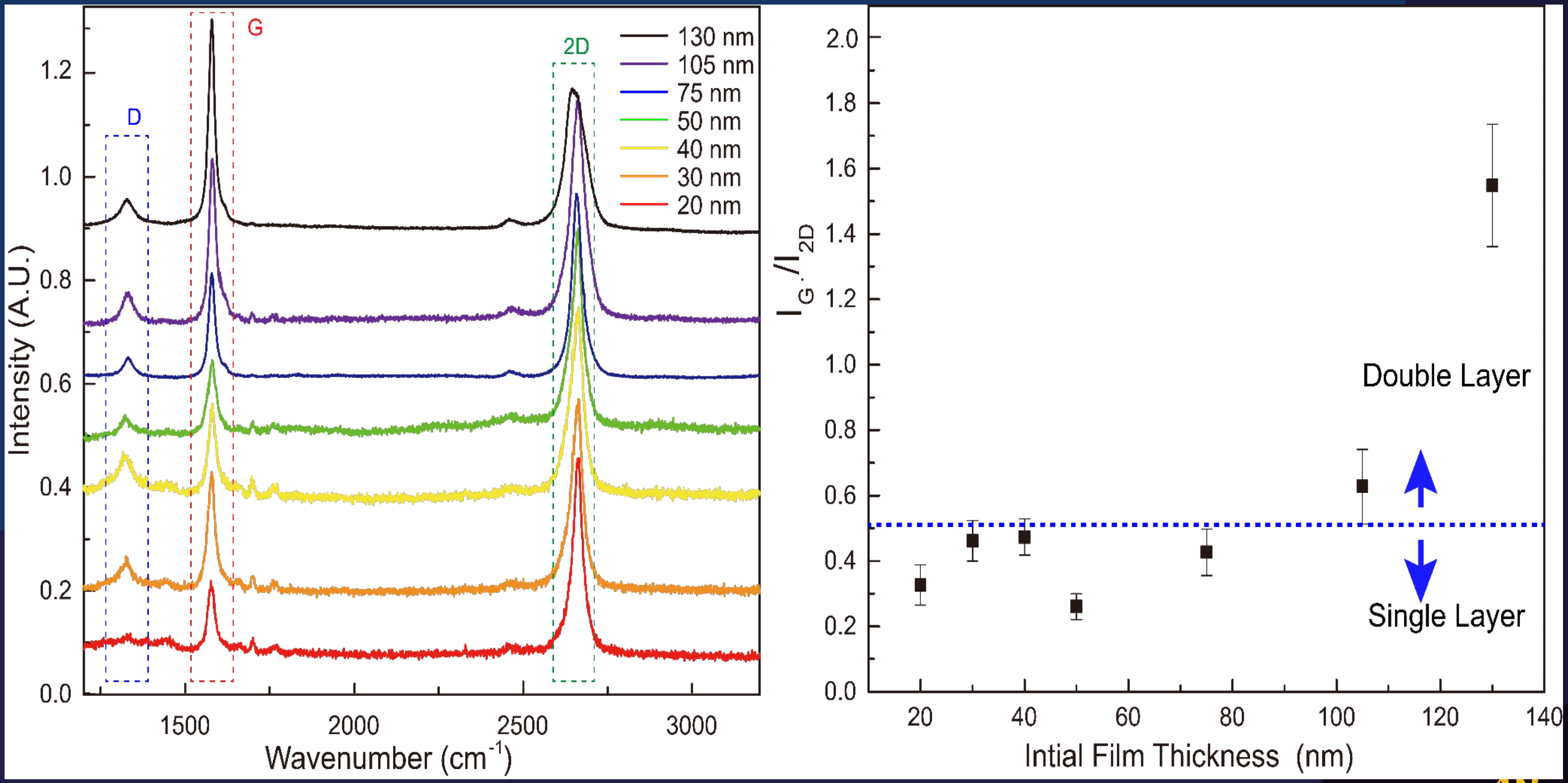


I_G/I_{2D} → graphene layer

I_{2D} → sp2 bond of graphene

Raman -Graphene on Ni Droplets

- Ni film thickness <105nm → single layer graphene
- Ni film thickness =130nm → double layer
- All graphene has low defects (low I_D)



Discontinuous Droplets, Continuous Graphene?

- **Under the right synthesis conditions →**

T (°C)	600	750	950	1000
	Ni	Ni	Ni	Ni
20nm	×	×	×	scattered
30nm	×	×	×	scattered
40nm	×	×	scattered	scattered
50nm	×	×	scattered	scattered
75nm	×	×	continuous	continuous
105nm	×	×	continuous	continuous

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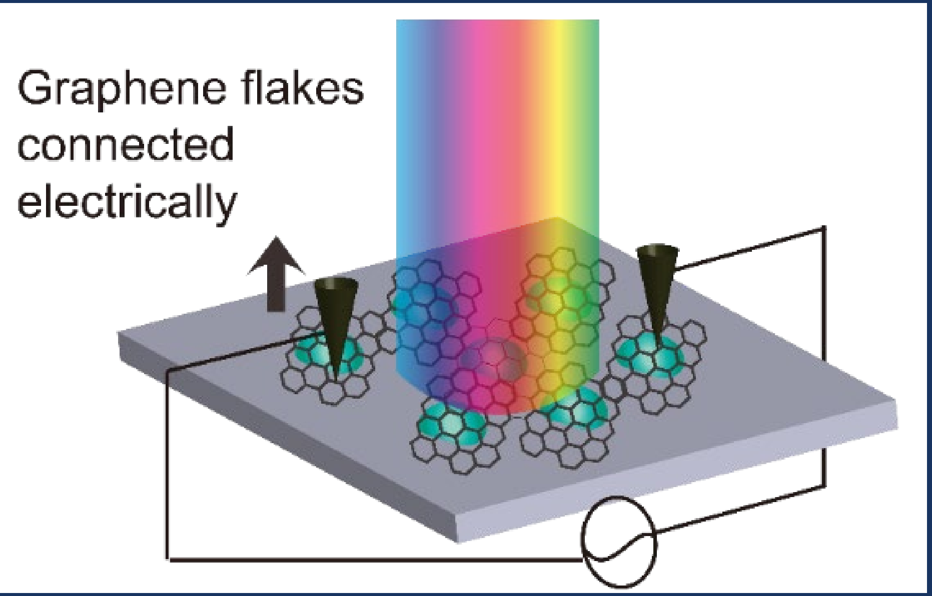
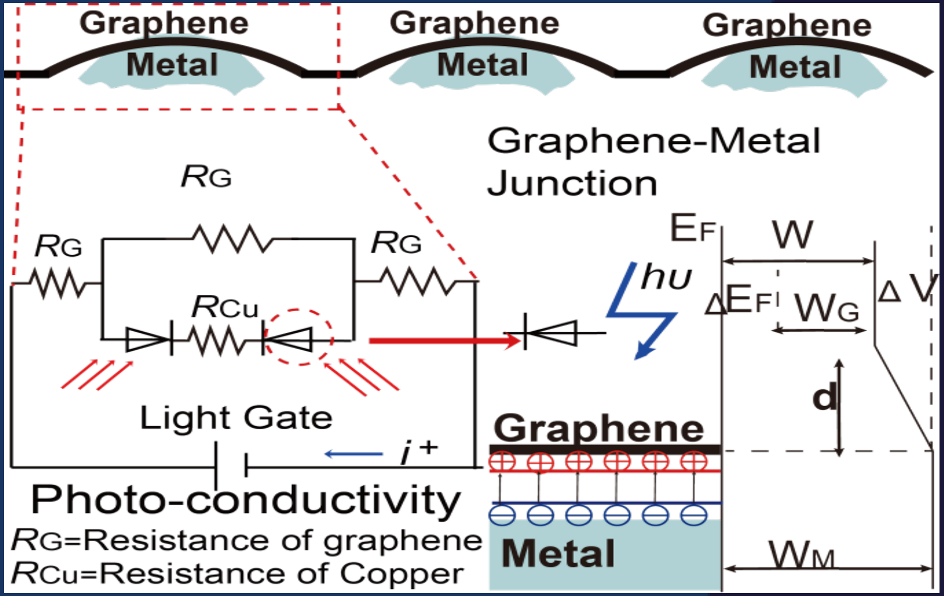
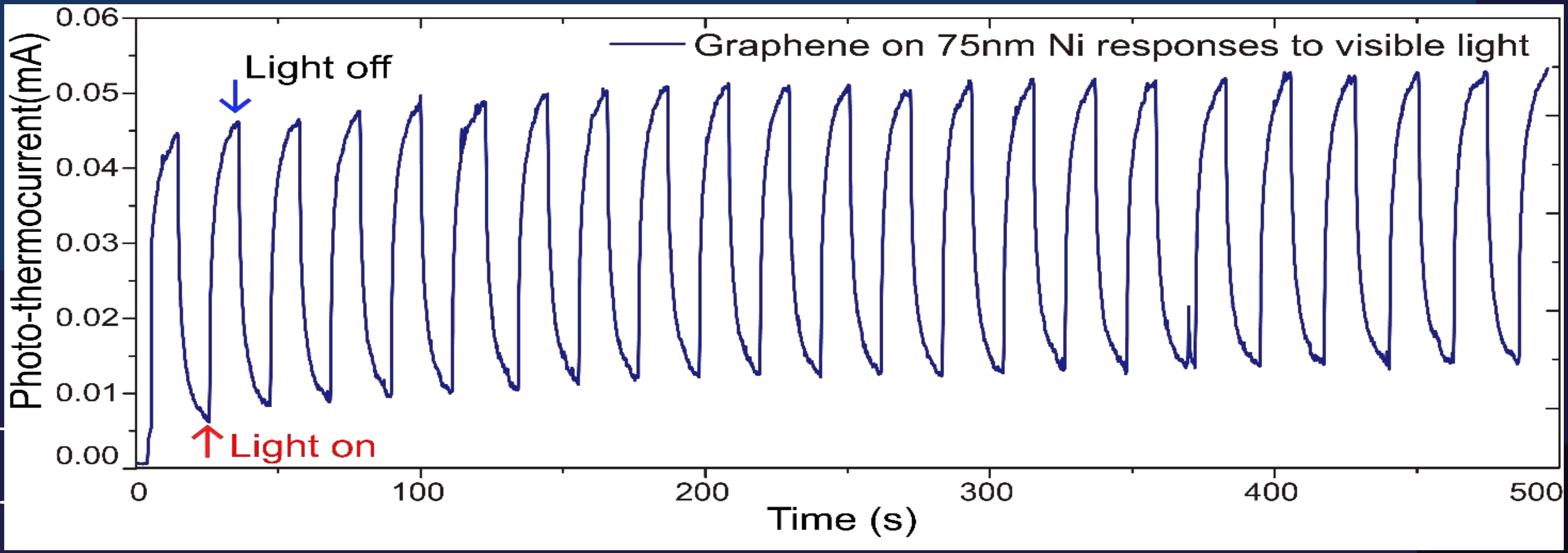
Application in Photonic Devices

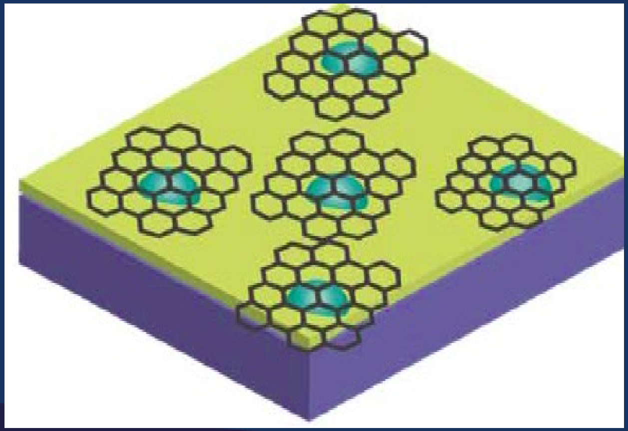




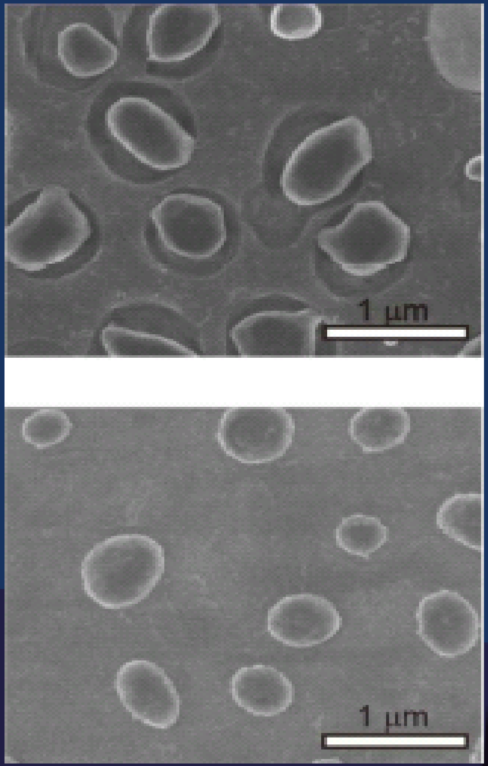


Short Summary

- **Large area graphene via multiple droplets?**
- **Continuous graphene with discontinuous metal?**
- **Controllability and process parameters?**
- **Quality of graphene film?**
- **Nickel or copper as the catalyst material?**
- **Potential applications?**



Synthesis by Multiple Droplets



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Outline

- Graphene synthesis by local CVD
  - Overview, synthesis methods, local CVD …
- Graphene synthesis by droplet CVD
  - Continuous graphene sheet? Application example ...
- Near-Field Electrospinning for Graphene based p- and n-type FETs
  - Electrospinning, graphene FETs, characterizations …

→Complementary graphene FETs based on the electrospinning process?

→Device demonstration?

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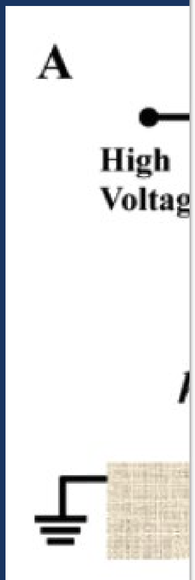
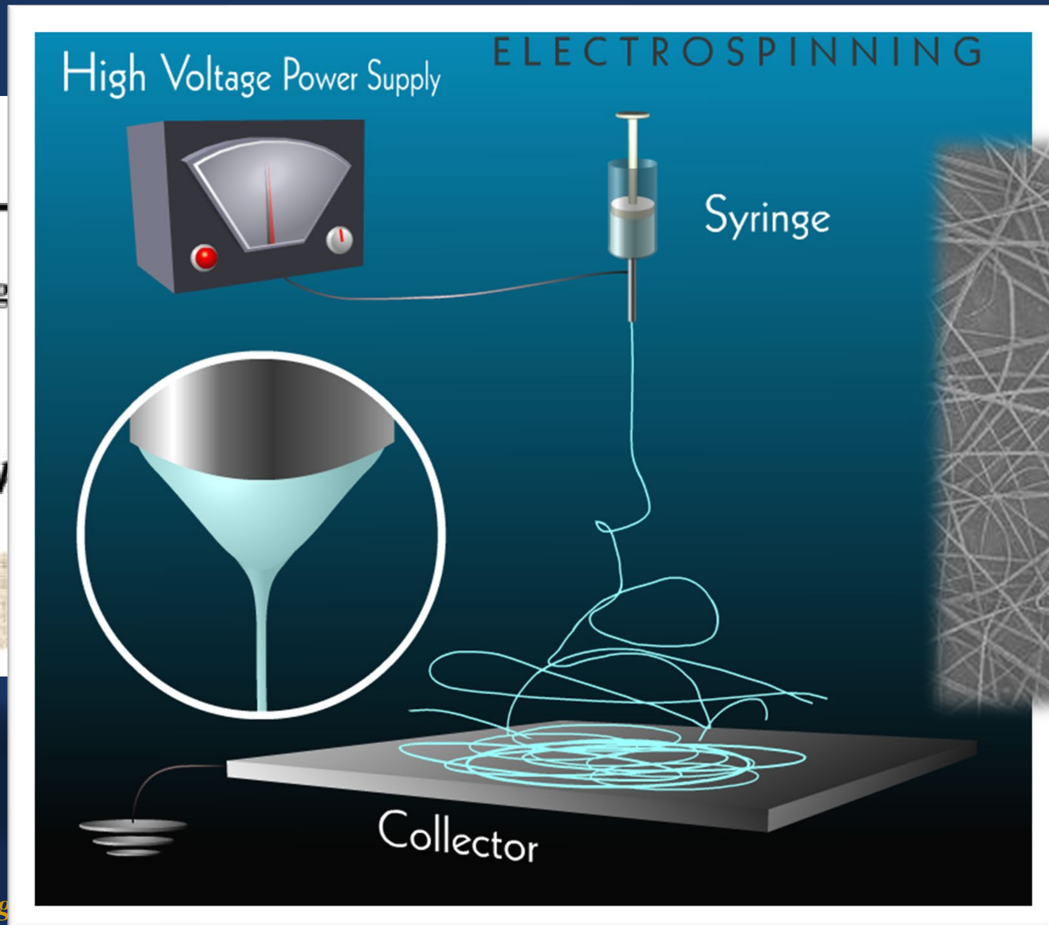
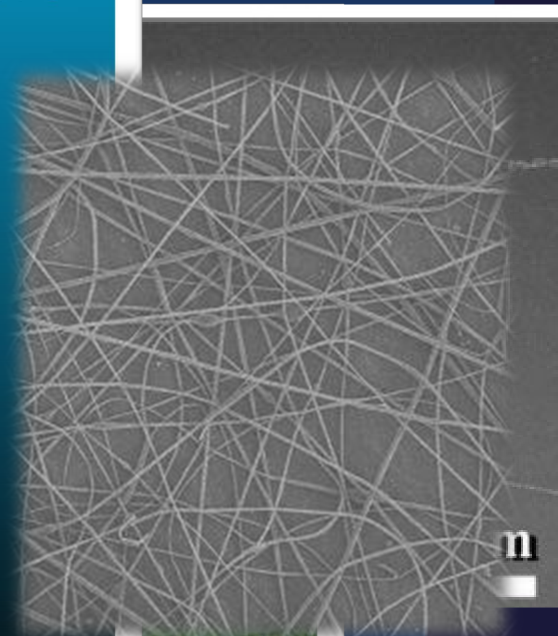
History & Research Background







DaoHeng ... Vol. 6, No. 4, pp. 839-842, 2006

Chieh Chang, Kevin Limkarilassiri and Liwei Lin, "Continuous Near-Field Electrospinning for Large Area Deposition of Orderly Nanofiber Patterns," Applied Physics Letters, Vol. 93, 123111, 2008

~20th century

~10th Century

Far-field electrospinning

Spinning wheel

http://nano.mtu.edu/electrospinning.htm

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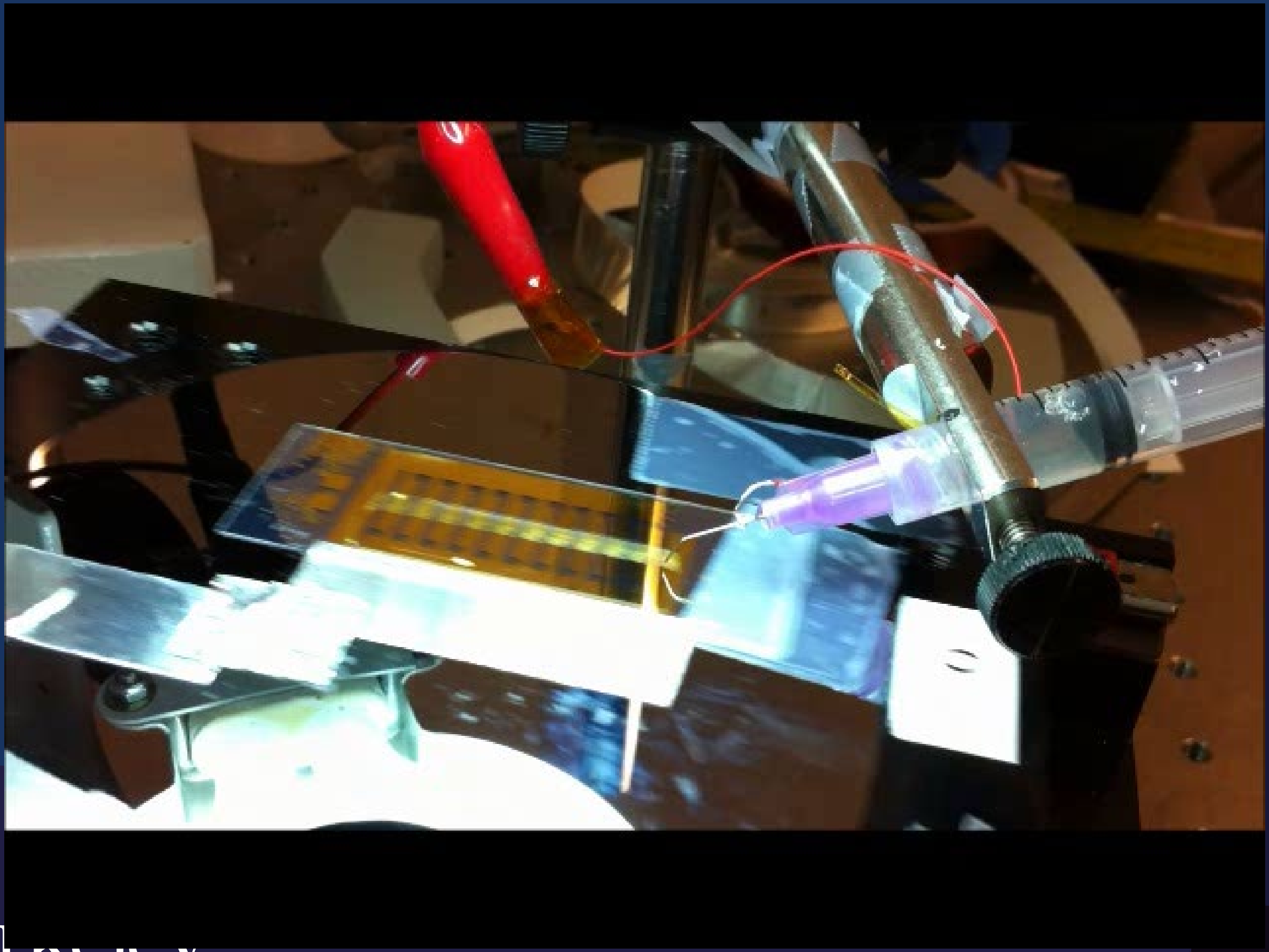
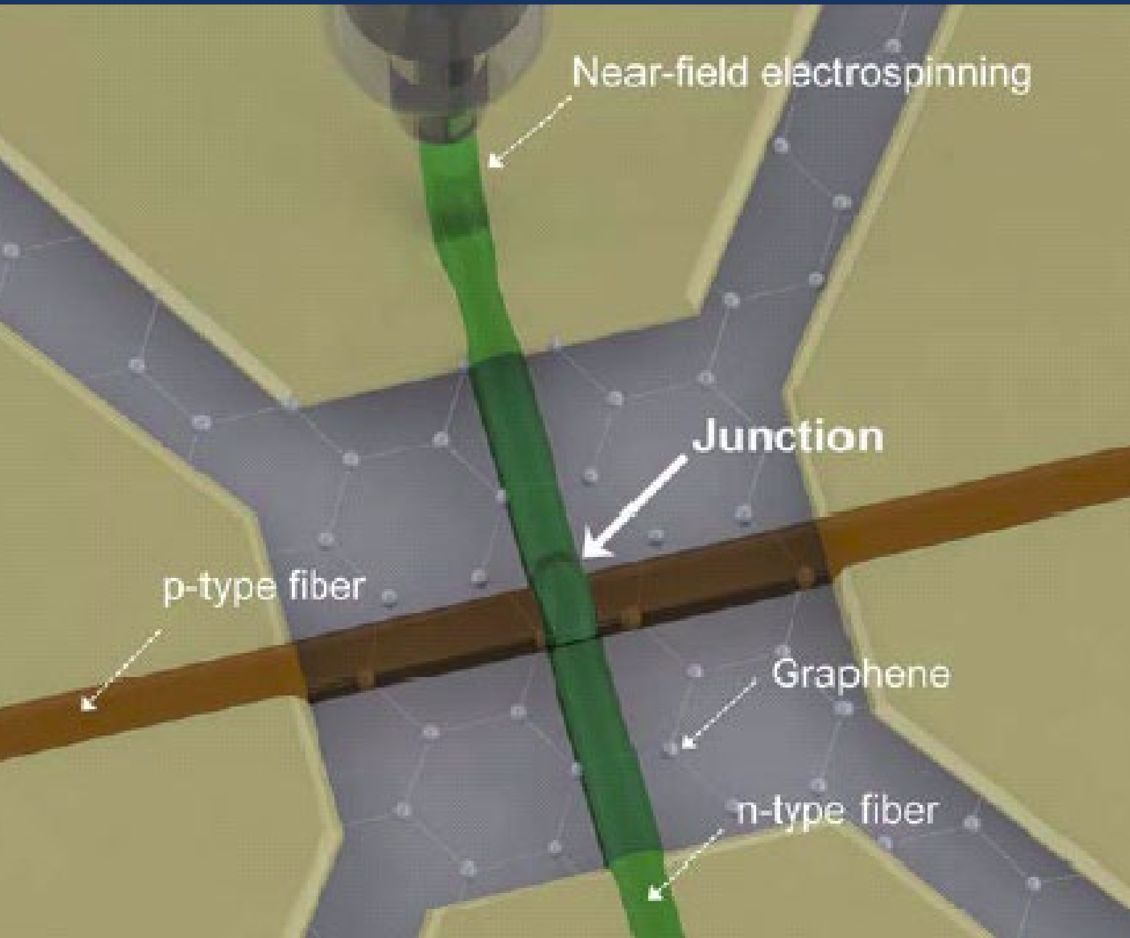
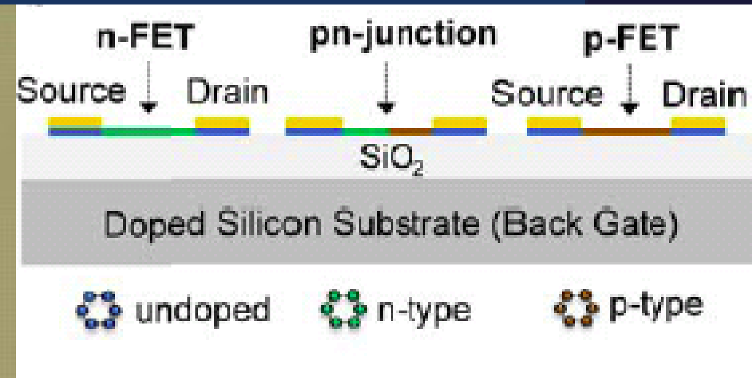
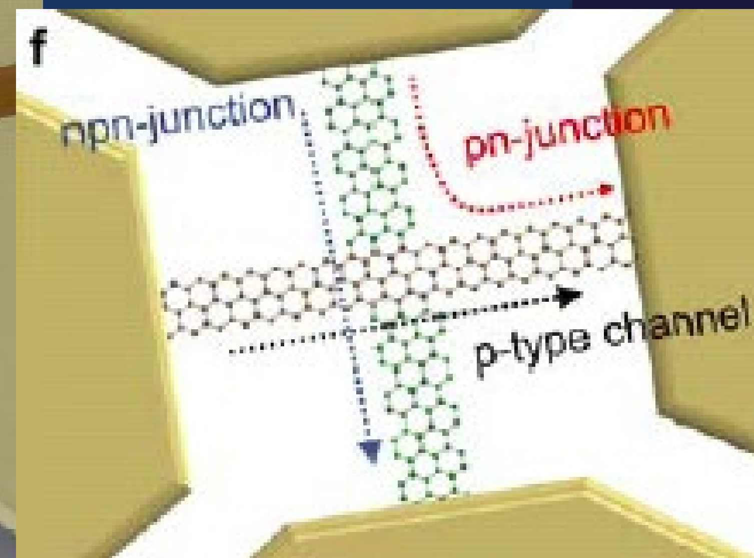
Near-field electrospinning - Video



Graphene-based Junctions







- **Junctions (pn, npn & pnp) and n-type, p-type graphene FETs can be fabricated by NFES in a very simple process**

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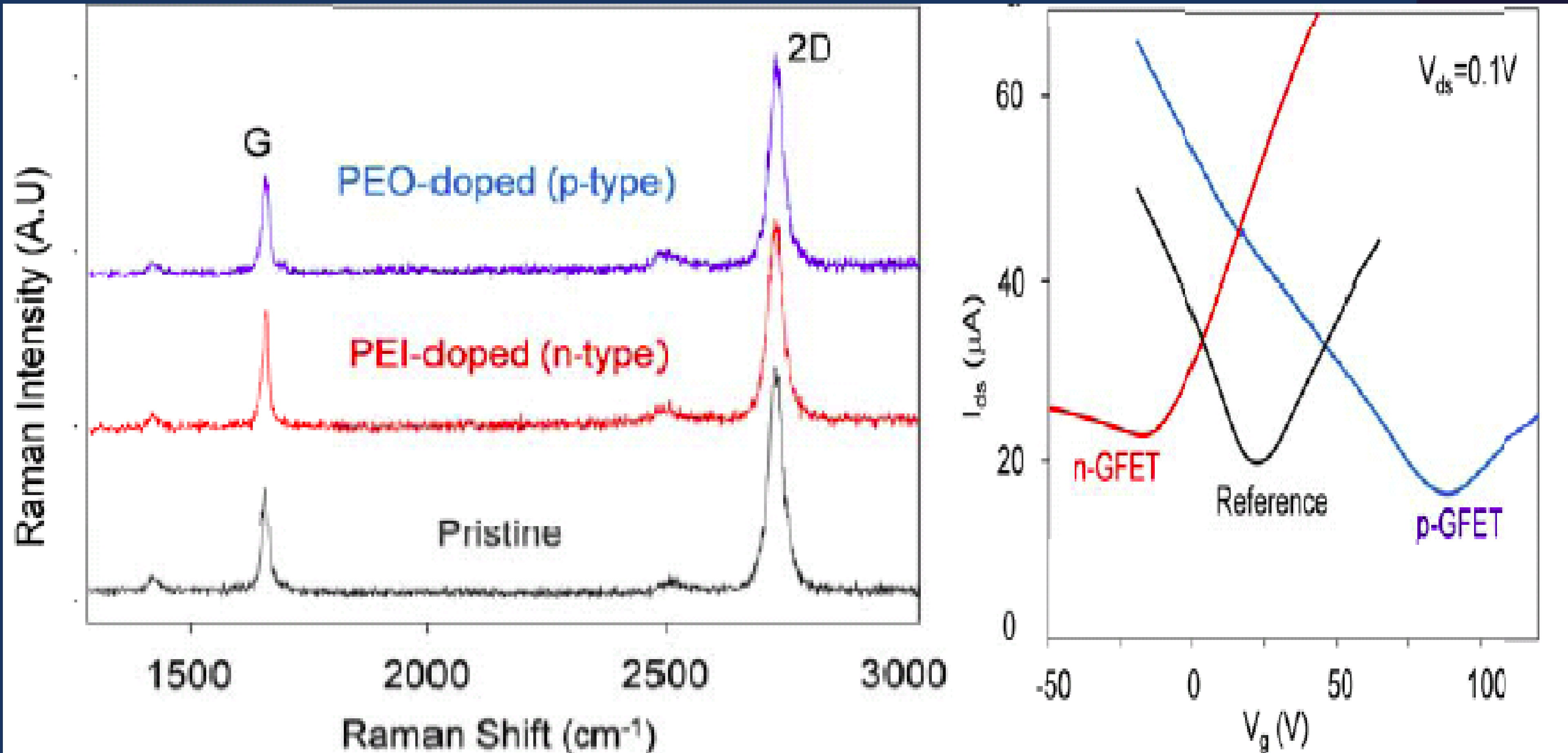
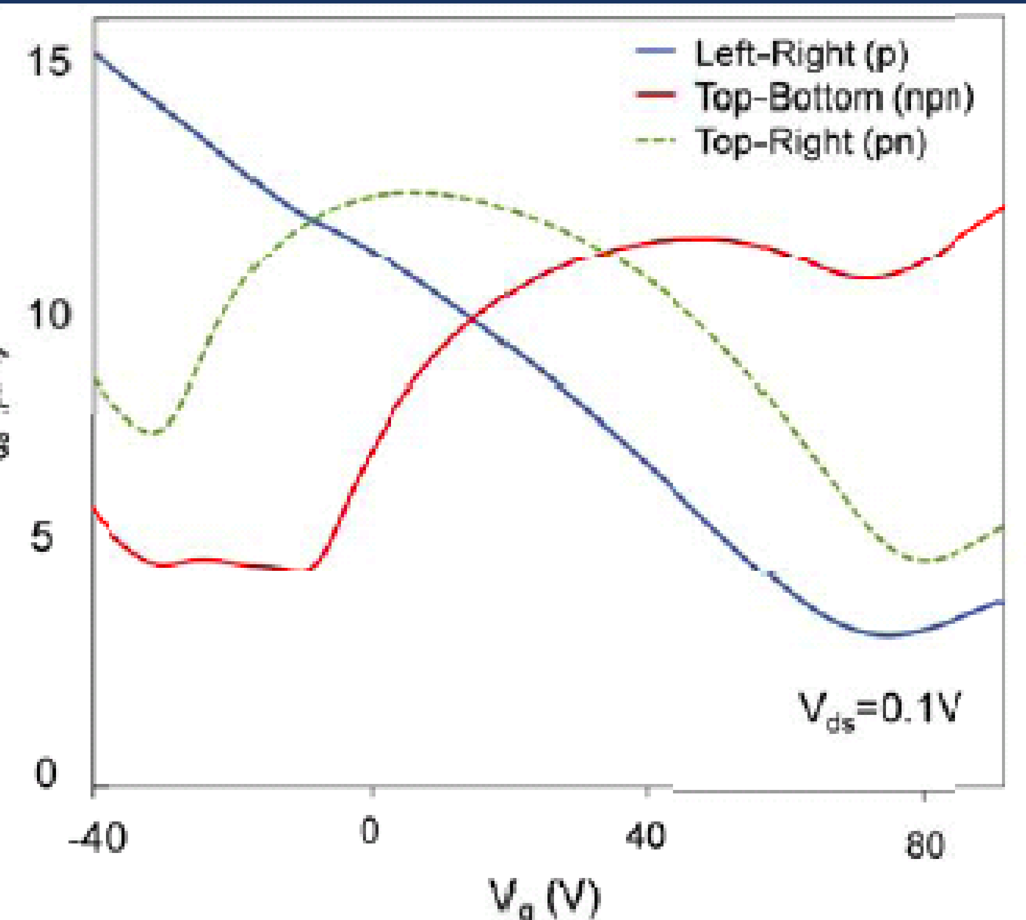
Jiyoung Chang, Yumeng Liu, Kwang Heo, Byung Yang Lee, Seung-wuk Lee and Liwei Lin, "Direct-write Complementary Graphene Field Effect Transistors and Junctions via Near-field Electrospinning," *Small* , Vol. 10, pp. 1920-1925, 2014.

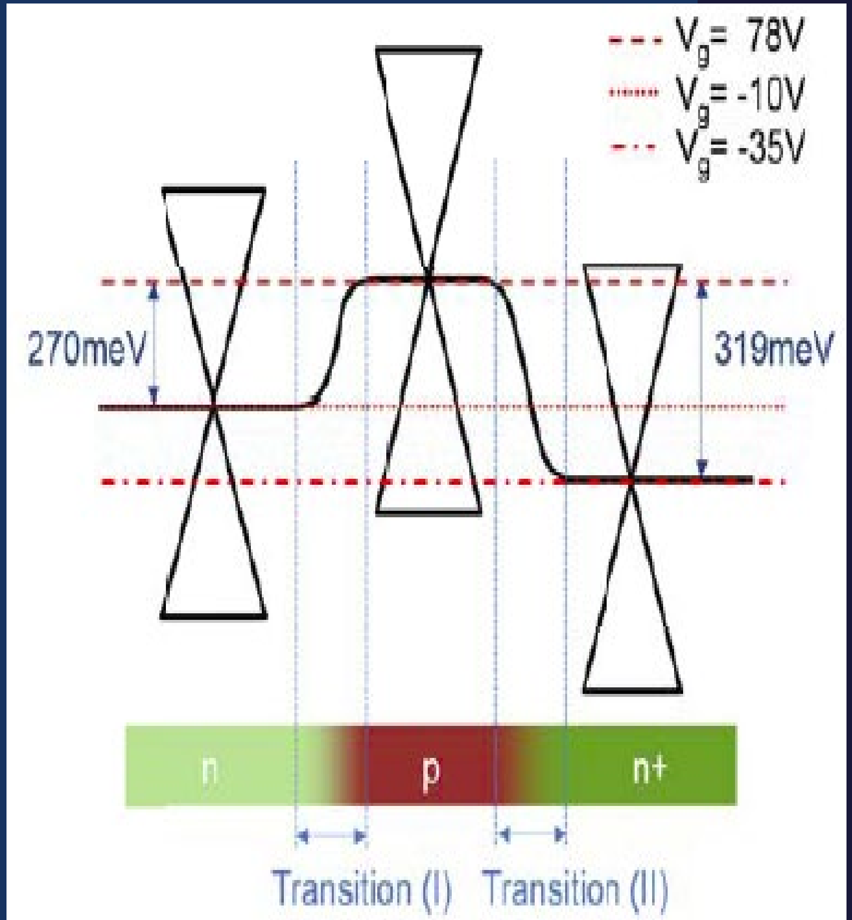
n- and p-type Graphene FETs



- **PEO** for d-type graphene FET, **PEI** for n-type graphene FET and **PVDF** for reference FET

Graphene pn & npn Junctions





- **Junctions (pn, npn) and p-type graphene FETs based on electrical wire connections all on the same simple device**

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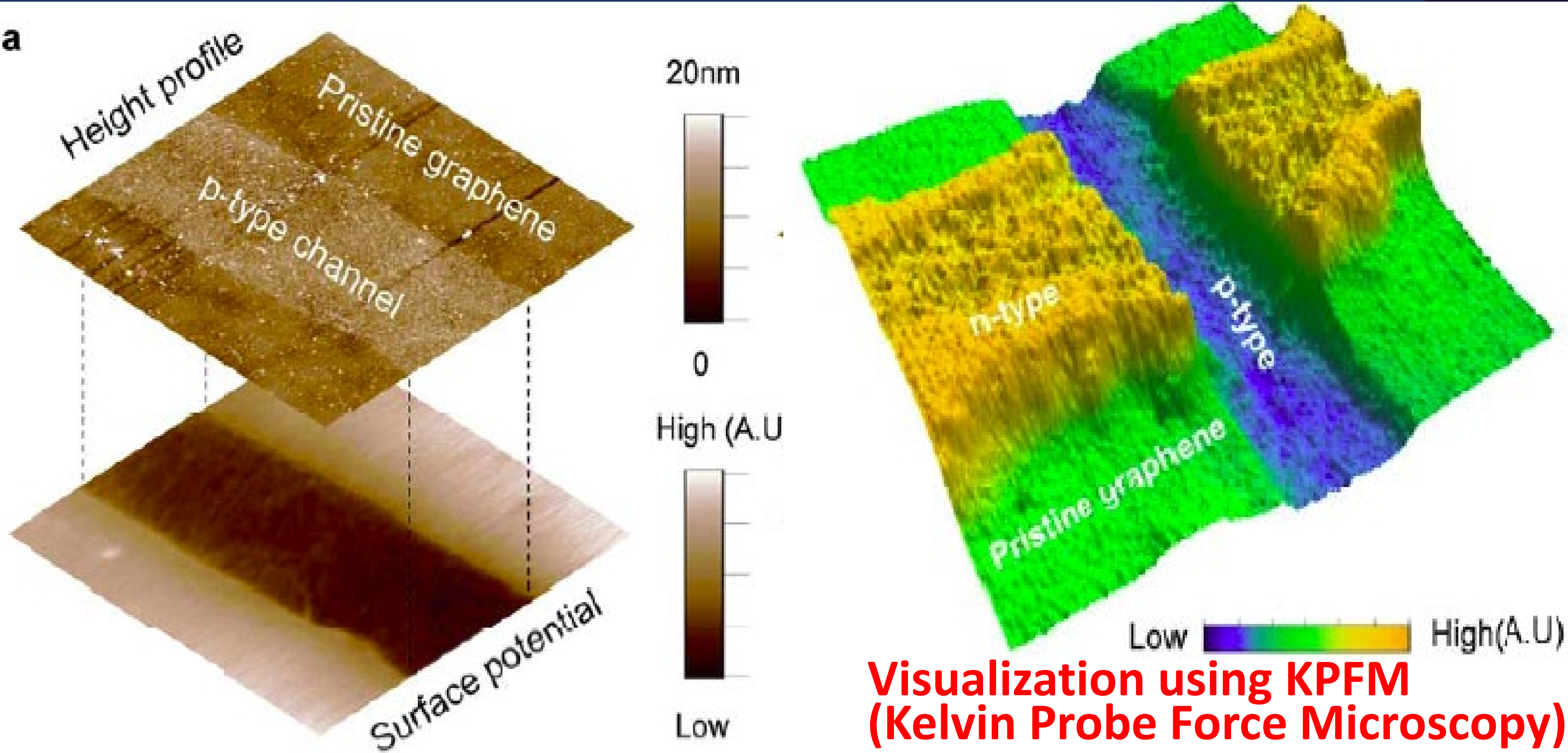
Potential Visualization by KPFM



Visualization using KPFM
(Kelvin Probe Force Microscopy)

- **AFM surface height characterizations & KPFM surface potential characterizations**

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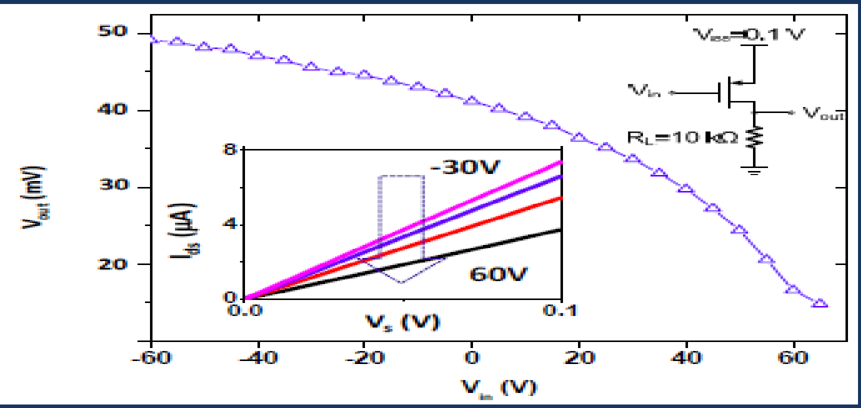
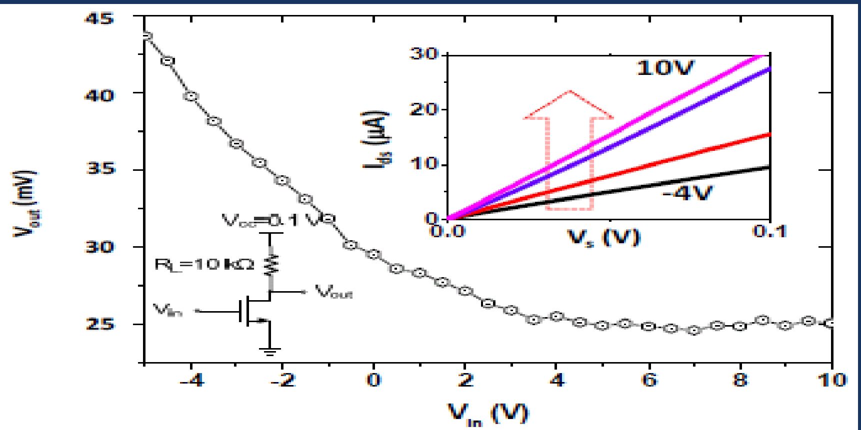
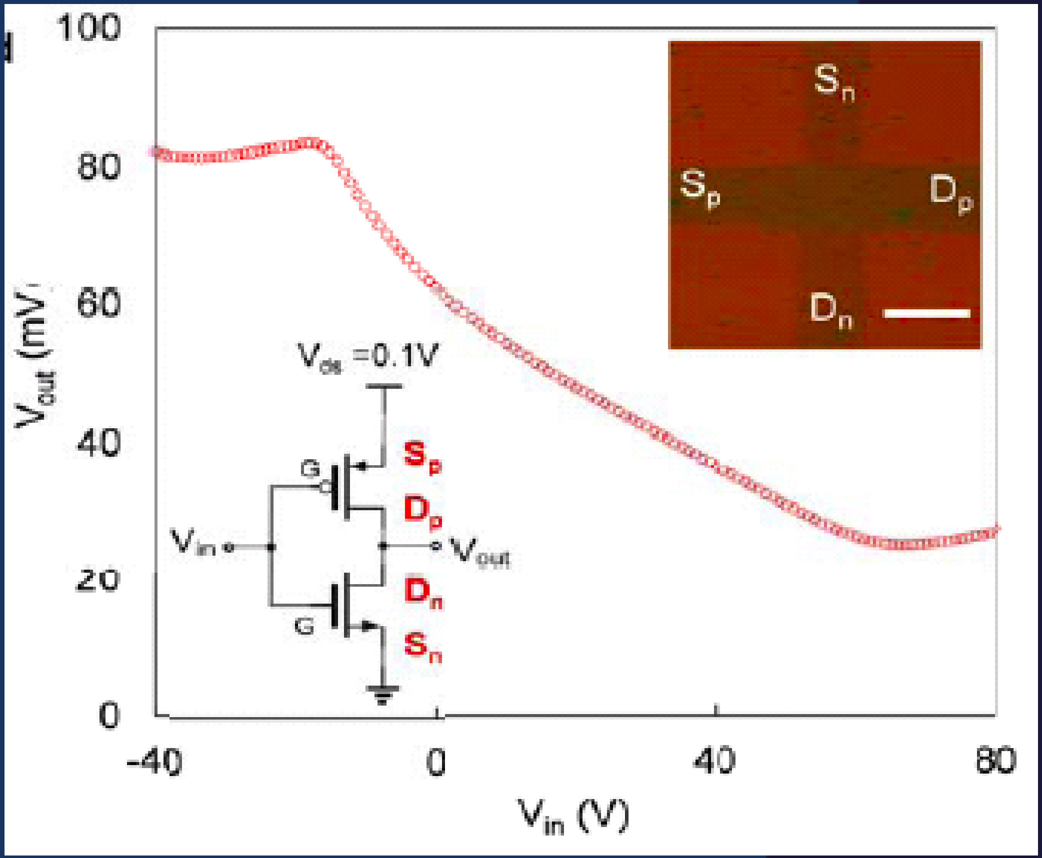
Working Graphene Device







- **Inverter of p-GFET** has ratio of 3.42 under -60 to 60V and **inverter of n-GFET** has ratio of 1.92 under -5 to 10V. **Complementary inverter** has ratio of 4.2.

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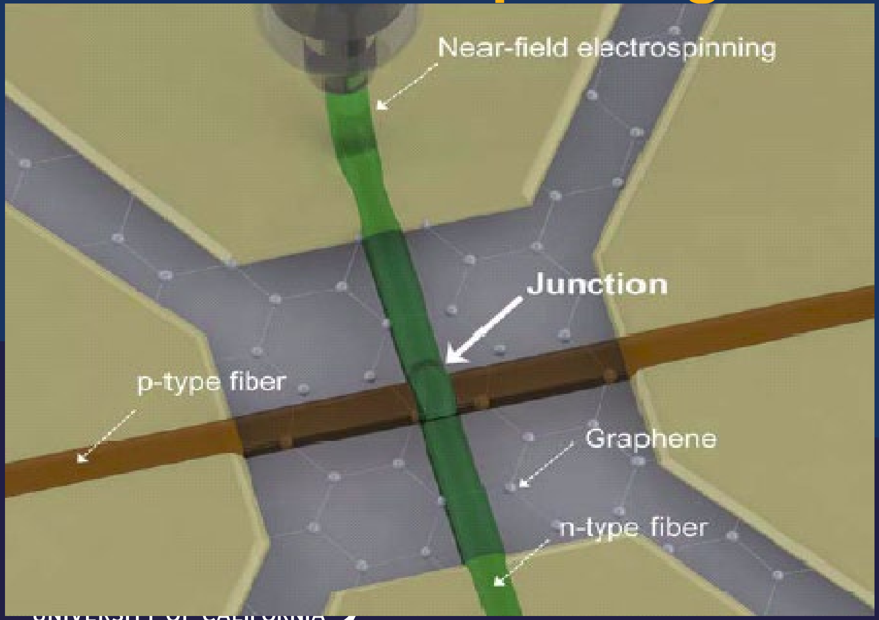
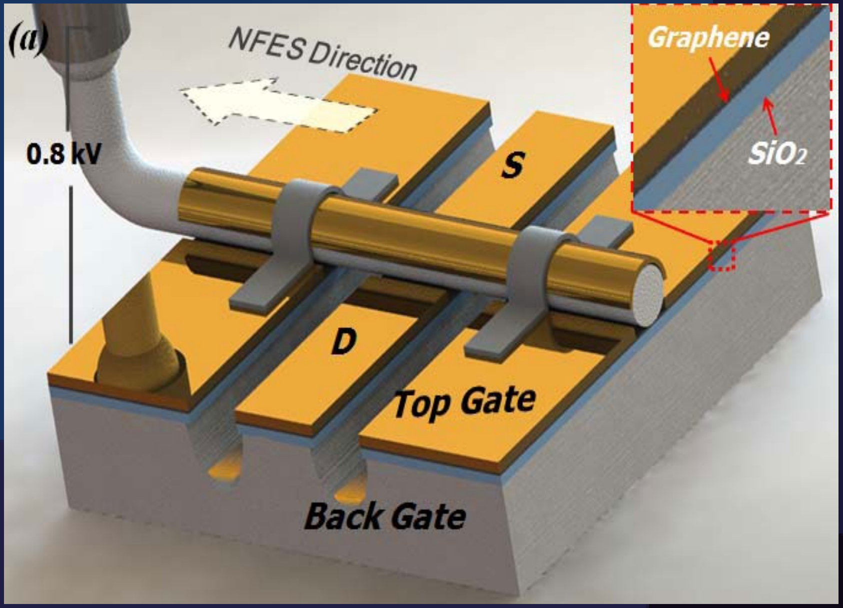
Short Summary

1. **Direct-write graphene FET by near field electrospinning**
2. **Direct-write graphene junctions and complementary n- and p-type FETs on the same substrate**
3. **Demonstration of simple graphene inverters**
4. **Both back-gate and front-gate graphene FETs by near field electrospinning**





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