Introduction to Nanotechnology and Nanoscience – Class#24

Liwei Lin

Professor, Dept. of Mechanical Engineering
Co-Director, Berkeley Sensor and Actuator Center
The University of California, Berkeley, CA94720
e-mail: lwlin@me.berkeley.edu
http://www.me.berkeley.edu/~lwlin

Outline

- Example for QD in biomedical application
- Paper 11
- 2D Materials - Graphene

OBITUARIES

Intel co-founder and philanthropist Gordon Moore has died at 94

March 25, 2023 · 5:57 AM ET

By The Associated Press

Elizabeth Holmes criminal fraud case starts today with jury selection

Alexis Keenan · Reporter

Tue, August 31, 2021, 5:15 AM · 3 min read

What was Theranos?

Founded in 2003, Theranos developed a portable device that it claimed could test for hundreds of illnesses using a single drop of blood. Inspired by the aesthetics of Apple products, Holmes poached designers from the tech giant to work on the "Edison" machine. Theranos promoted its blood-testing device as cheaper and more portable than traditional intravenous blood tests.

Ruling on Elizabeth Holmes' prison delay, restitution to Theranos investors pushed back

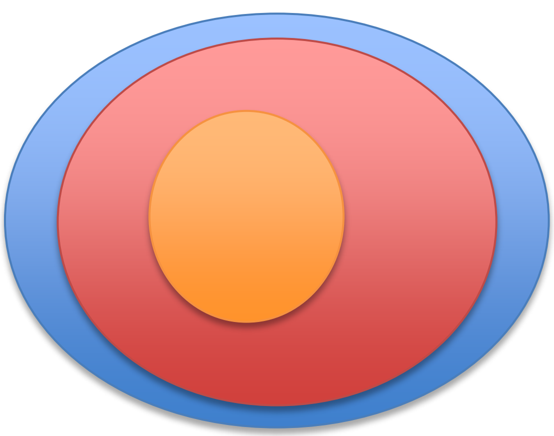
By Andrea Park • Mar 20, 2023 03:40pm

After a four-month trial ended in Holmes being convicted on four of 11 counts of defrauding investors at the start of 2022, she was sentenced in November to 11.25 years in prison plus three years of supervised release. The ex-CEO and founder of Theranos is appealing the conviction, and her lawyers have requested that she be allowed to stay out of prison until the appeal process is complete.

The Rest of the Semester

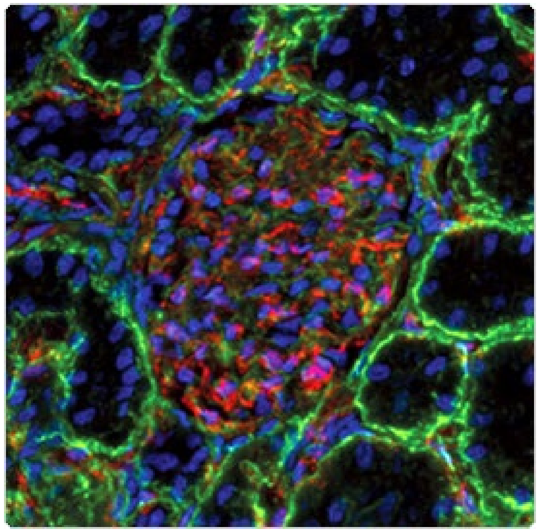
- 4/16 (next Tuesday) – Review for Quiz II
- 4/18 – Quiz II, close book, open 2-page cheating sheets
- 4/23 & 4/25, Final project presentations, extra slots on 4/29 & 4/30 (Monday & Tuesday) in the google sign-up sheet
- 5/5 Final project report due at bcourse

- The use of semiconductor nanocrystals: problematic；
- The high surface area of the nanocrystal might lead to reduced luminescence efficiency and photochemical degradation;
- Solution: By enclosing a core nanocrystal of one material with a shell of another having a larger bandgap
- BUT, soluble only in nonpolar solvents
- By adding a third layer of silica that makes the core-shell water soluble



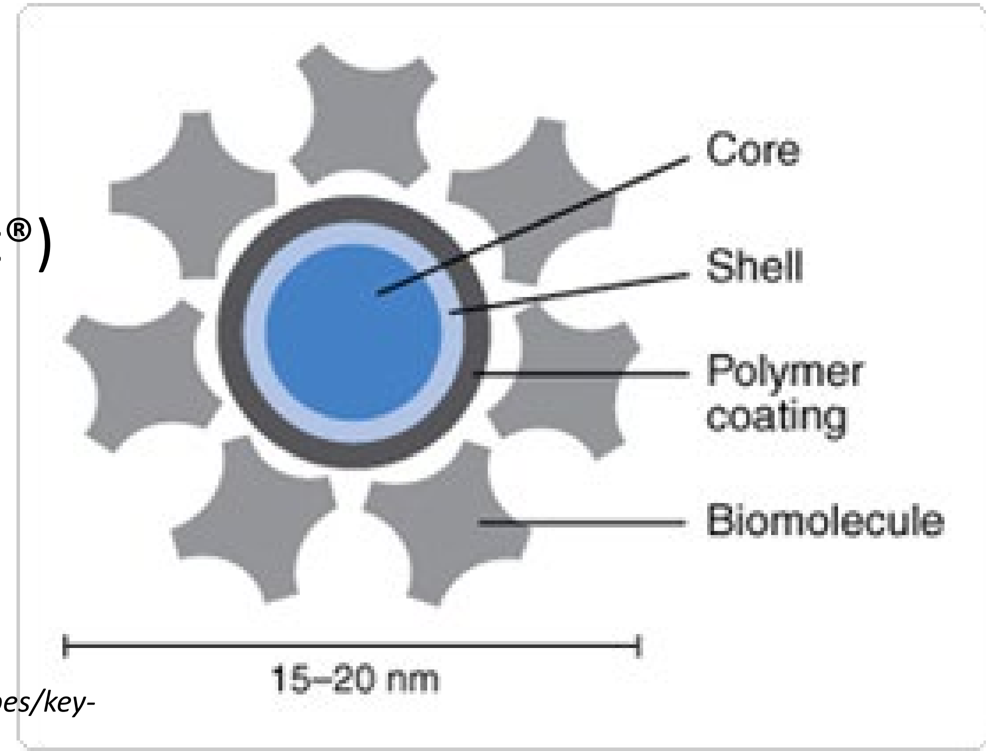
Orange: Fluorescent nanocrystals
Red: material with a larger bandgap
Blue: silica

Applications



- As predicted by this 1998 paper:
  - Multicolor biological experiments and diagnostics
  - Cytometry and immunocytobiology
  - X-ray fluorescence, x-ray absorption, electron microscopy, scintillation proximity imaging
  - Infrared dyes

  - Commercially available (Qdot®)
  - Multispectral flow cytometry
  - Cell tracking
  - Cell/tissue staining
  - *In vivo* imaging

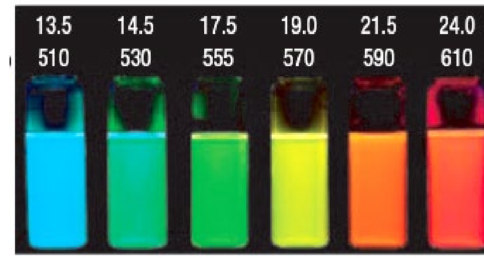


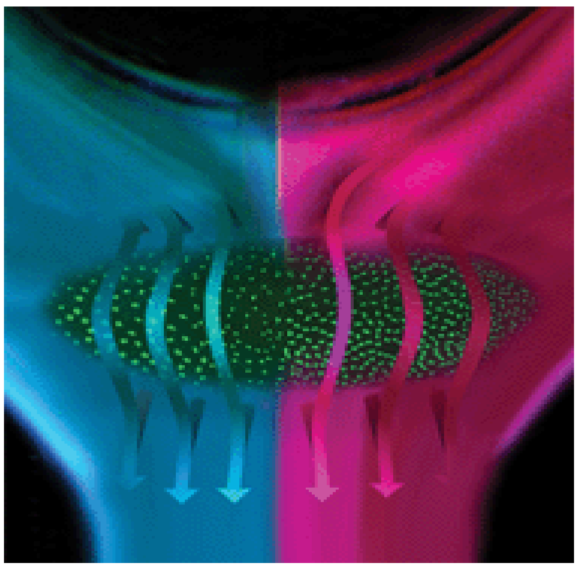
Bruchez, M. *et al*. *Science* **1998**, 281, 2013-2015.
https://www.thermofisher.com/us/en/home/brands/molecular-probes/key-molecular-probes-products/qdot.html

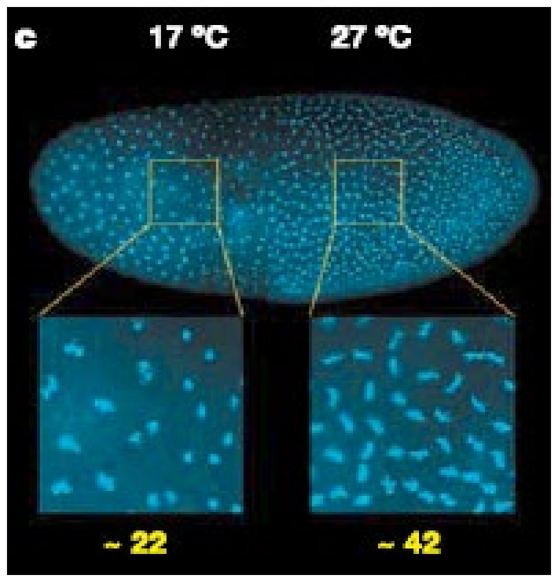
Introduction – QD as Thermometers

Temperature response to the environmental variations and/or cells response to environmental temperatures

ex: cold exposure, heat shock, thermogenesis…







E. M. Lucchetta, M. S. Munson, R. F. Ismagilov, *Nature* 434, 1134 (Apr, 2005)

- **Pros**
  - Photostability
  - Broad absorption, narrow emission
  - Long fluorescence lifetime
  - Tunable spectra
- **Cons**
  - Blinking

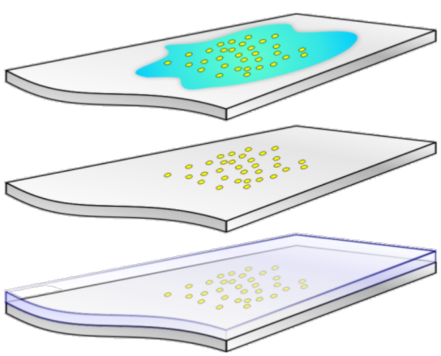
Single QDs Temp. Characterization

⦿CdSe QDs (Qdots/Invitrogen)

- Encapsulated by a ZnS shell
- Coated with organic polymer, and streptavidin conjugated

⦿Sample Preparation

- QDs solution was diluted in PBS
- Coat on cover-slips and dry
- Fix QDs by PDMS

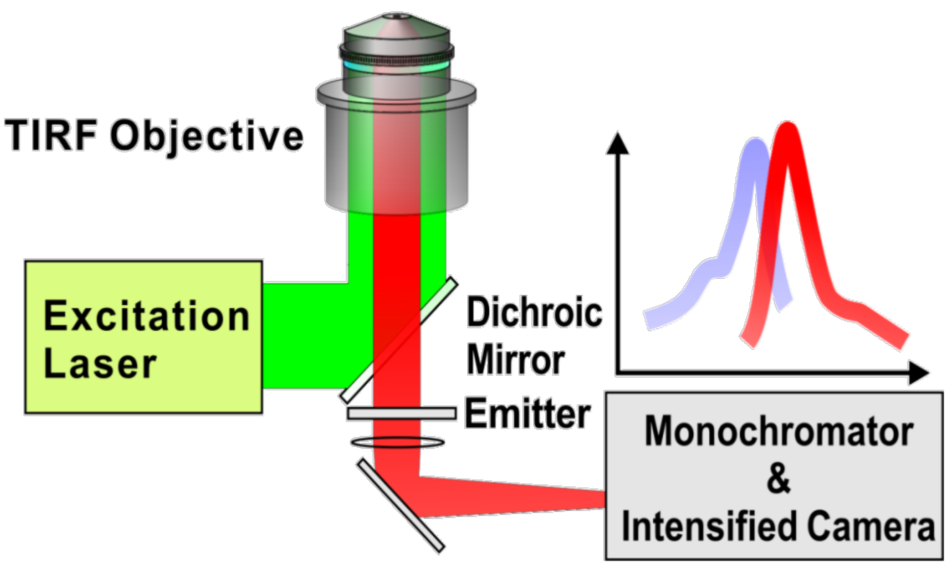


⦿Temperature Control

- Heated water bath

⦿Optical Setup

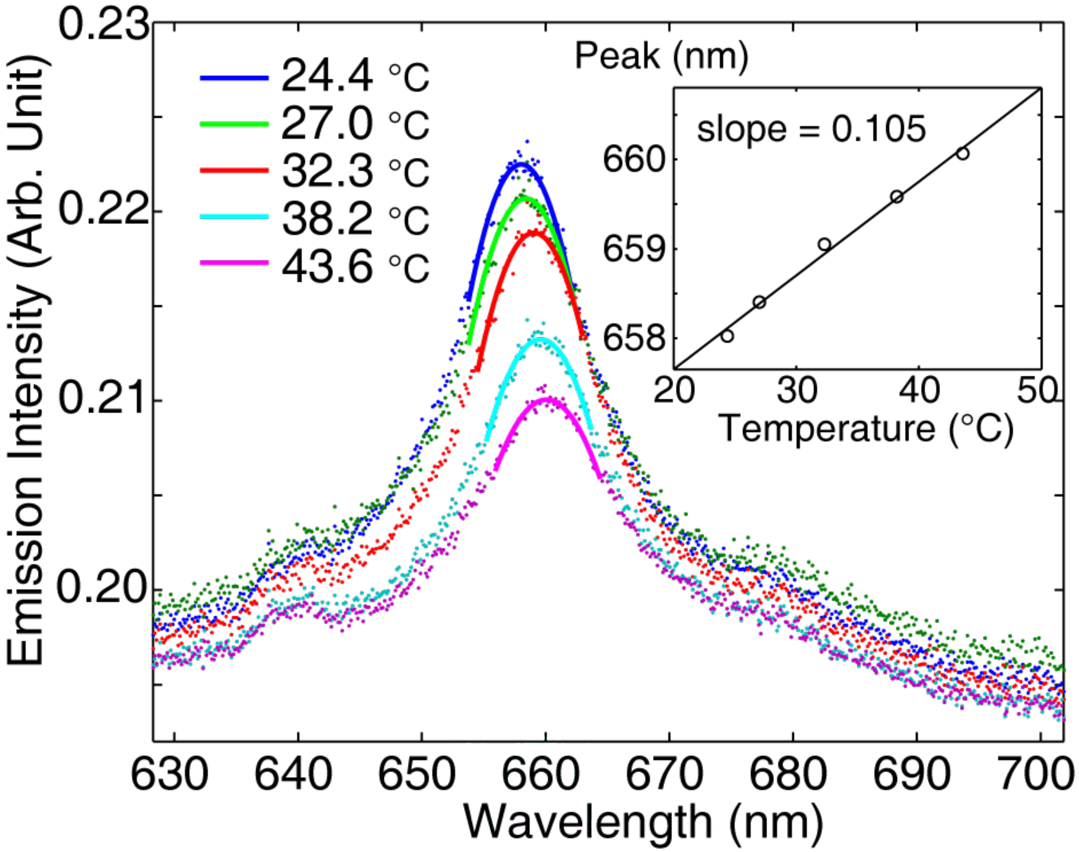
- 532-nm CW laser
- 100X/1.45 TIRF objective

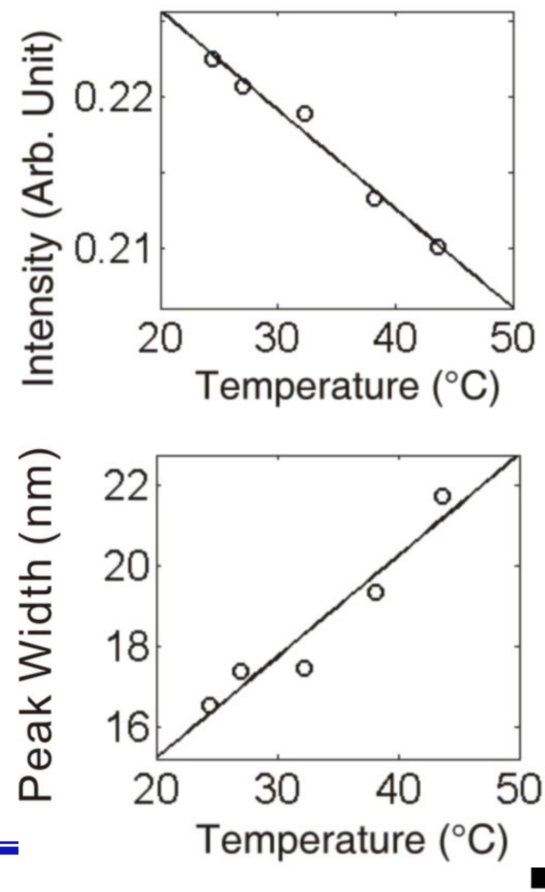


Measurement Results

⦿Peak Spectrum Shift

- Peak wavelength of QD exhibits a red shift as temperature increases
- Intensity decreases with increasing temperature.
- Full width at half maximum (FWHM) increases as temperature rises



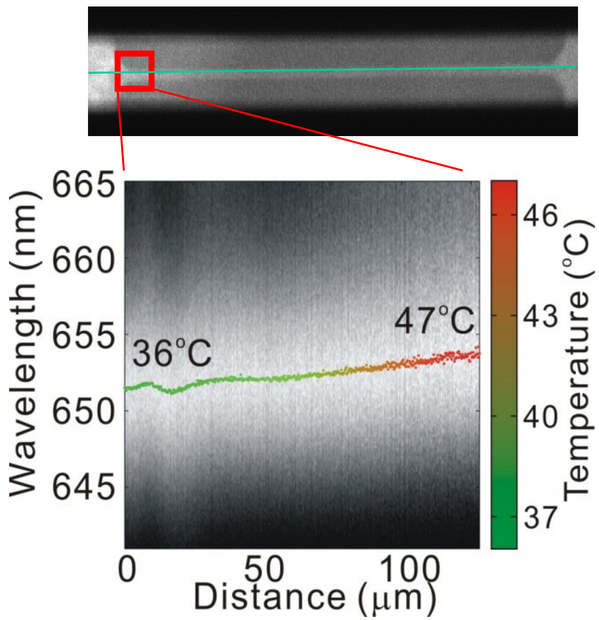


Example #1 - MEMS Device Temperature

Nanoletters, Vol. 7, pp. 3102-3105, 2007

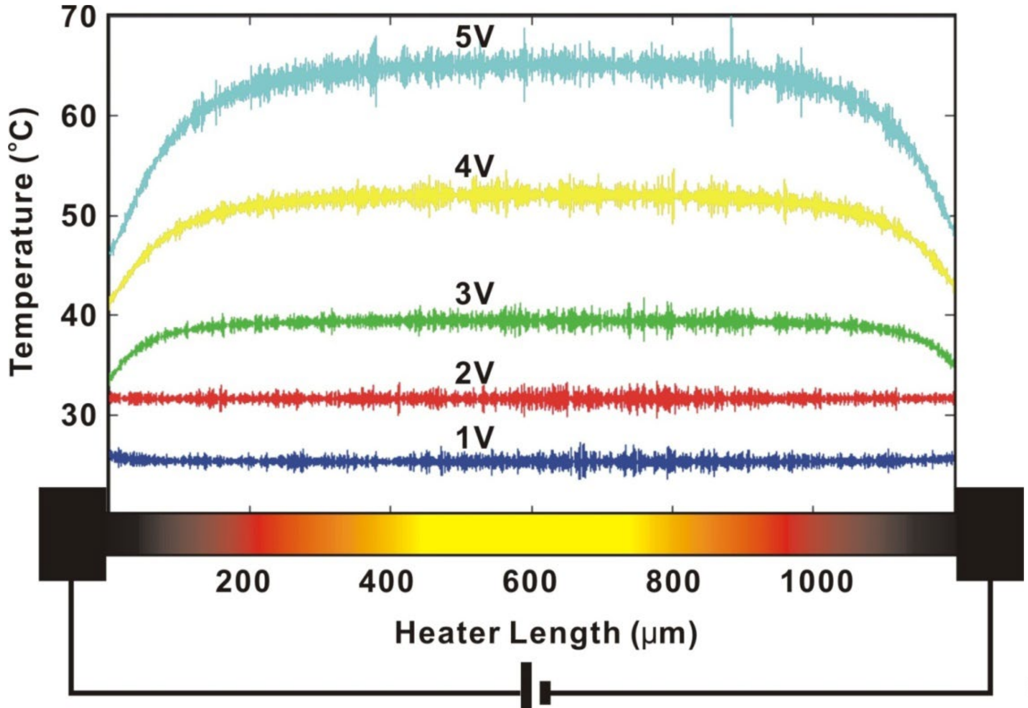
- **MEMS Heater Temperature Measurement**
  - Joule Heating Element
  - Metal Line Heater (Al) 1200 x 40 um

Fluorescent image with QDs coating



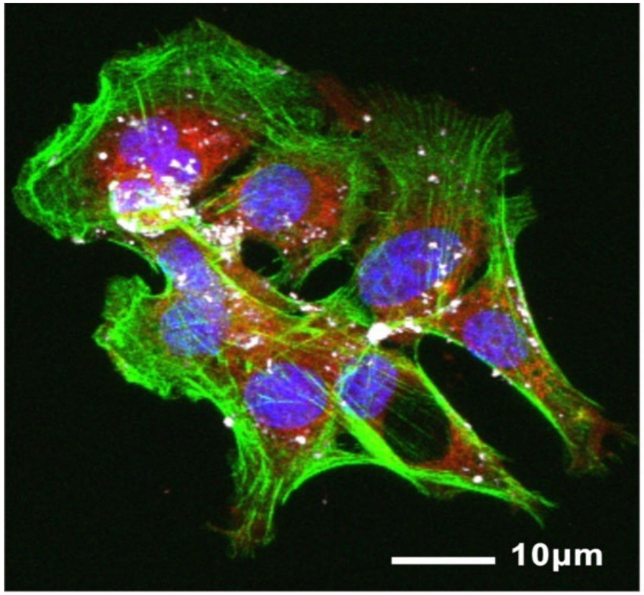
steady state solution:

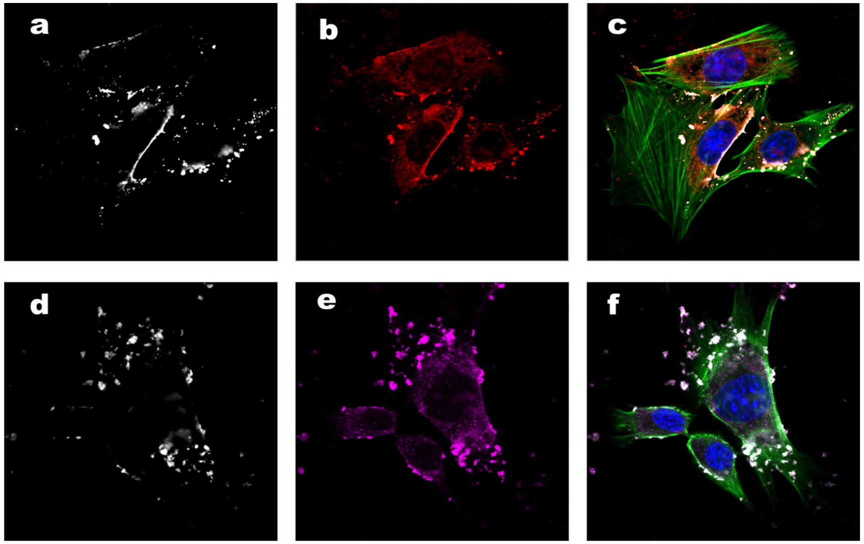
$$T(x) = T_r - (T_r - T_\infty)\frac{\cosh[\sqrt{\varepsilon}(x - L/2)]}{\cosh(\sqrt{\varepsilon}L/2)}$$

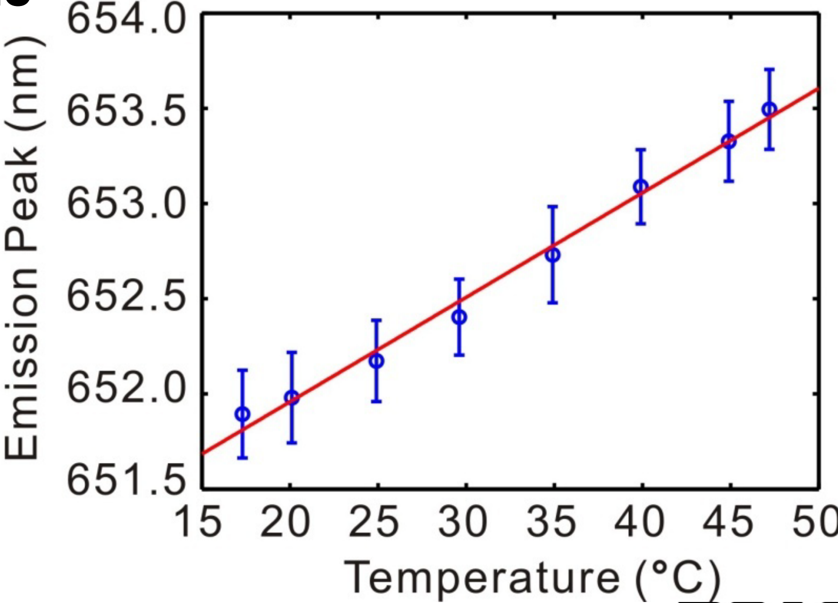


Example #2 - Intracellular Temperature

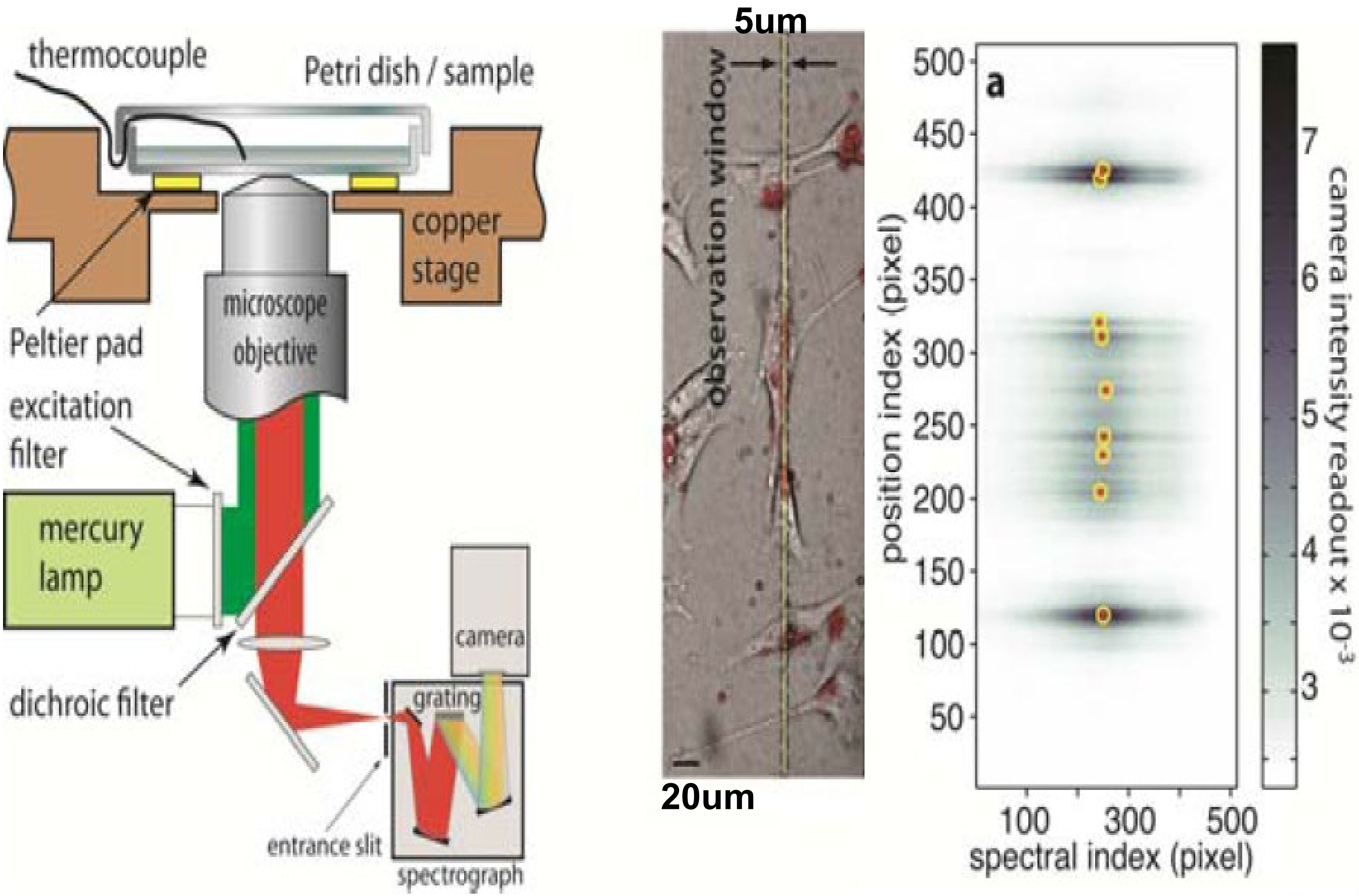
- ⦿655nm CdSe QDs (Molecular Probes)
- ⦿Endocytosis QDs into NIH/3T3 cells
- ⦿Multicolor Labeling
  - Red: mitochondria
  - Green: actin filaments
  - Blue: nuclei
  - White: quantum dots (temp. markers)
- ⦿ Confocal Fluorescent Micrographs







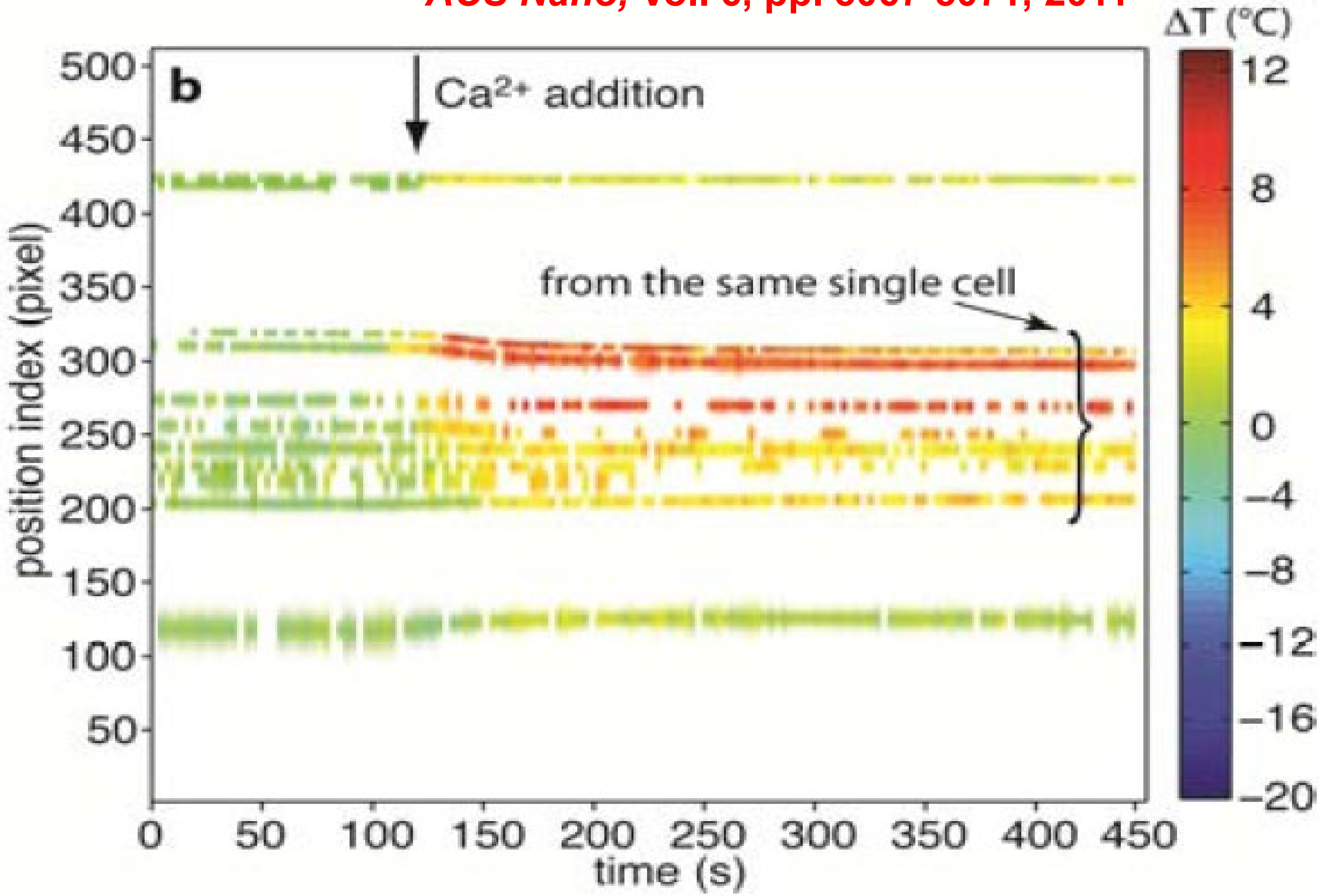
Experimental Setup



BSAC

Test #1 Thermogenesis by Calcium

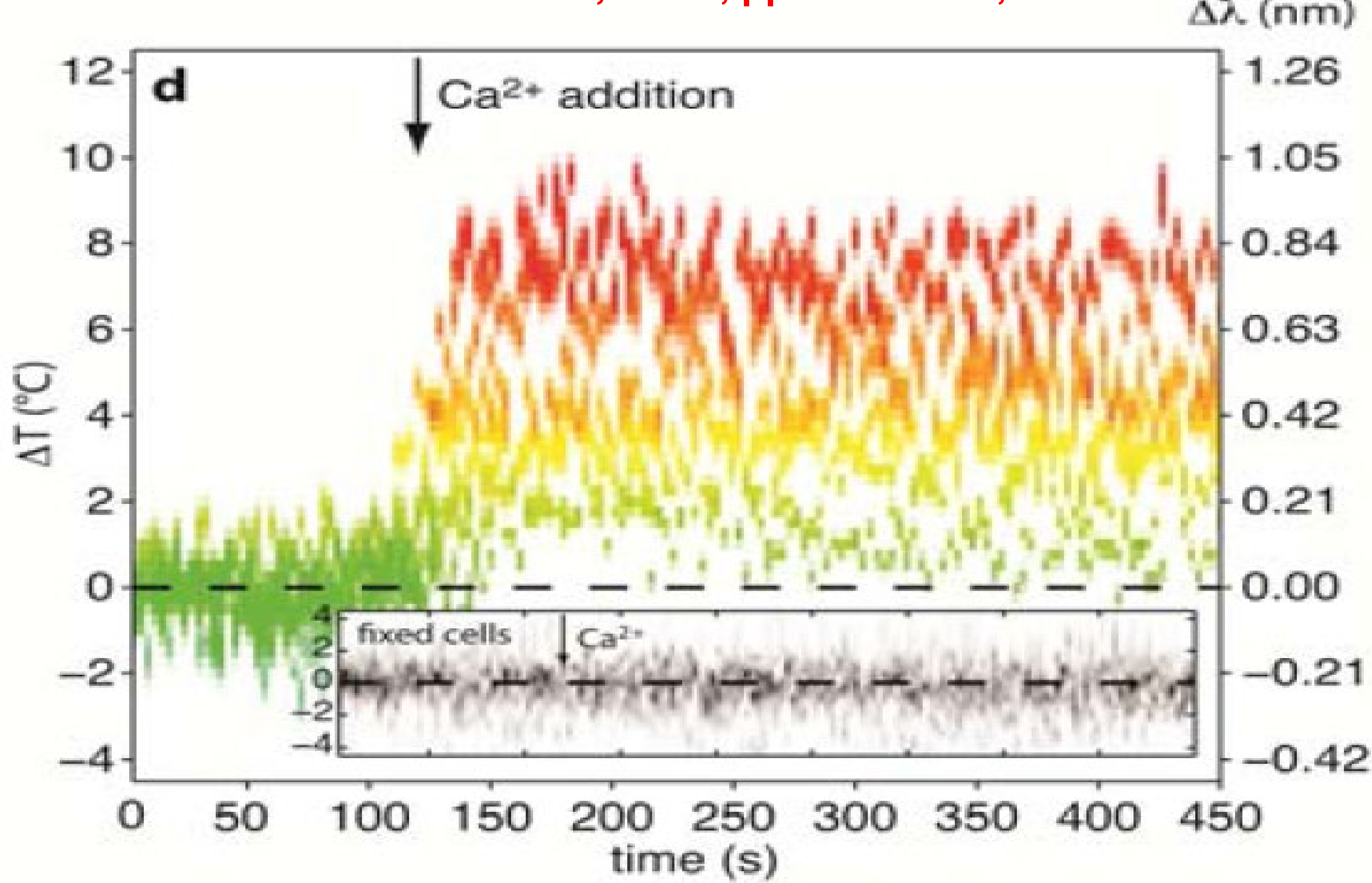
ACS Nano, Vol. 6, pp. 5067-5071, 2011



BSAC

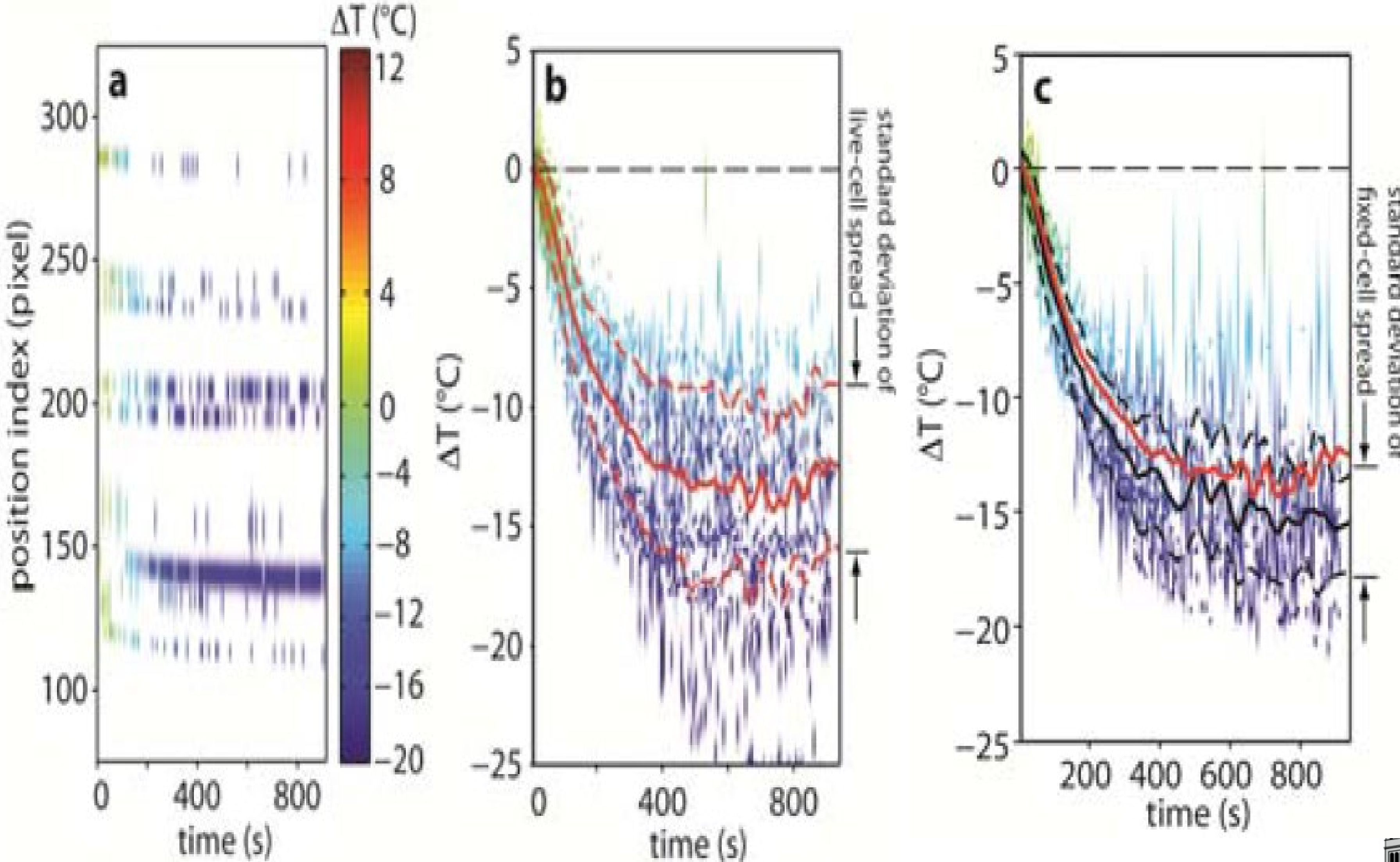
Test #1 Thermogenesis by Calcium

ACS Nano, Vol. 6, pp. 5067-5071, 2011



BSAC

Test #2 Thermogenesis by Cold Shock



Short Summary

- The spectral shift of a single quantum dot was successfully characterized as 0.1 nm/^{o}C at room temperature range.
- Transient temperature distribution within a single living cell has been measured. NIH/3T3 cell lines have reacted to maintain their physiological temperature under cold exposure.
- Long term goal: studies of intracellular local temperature responses/characteristics in living cells for fundamental biological processes and diagnostics

Background

- Surface Plasmons (SPs): Waves that ride along the surface of a conductor. Their interactions with the surface's free electrons allow them to confine light.
- SPs interactions with light are at the nanometer scale and show great potential for different applications
    - Optics, data-storage, microscopy, sensors.
- Scientists are increasingly interested in SPs due to advancements in the field of nanotechnology that allow for further manipulation of SP properties.

Basics of Surface Plasmons

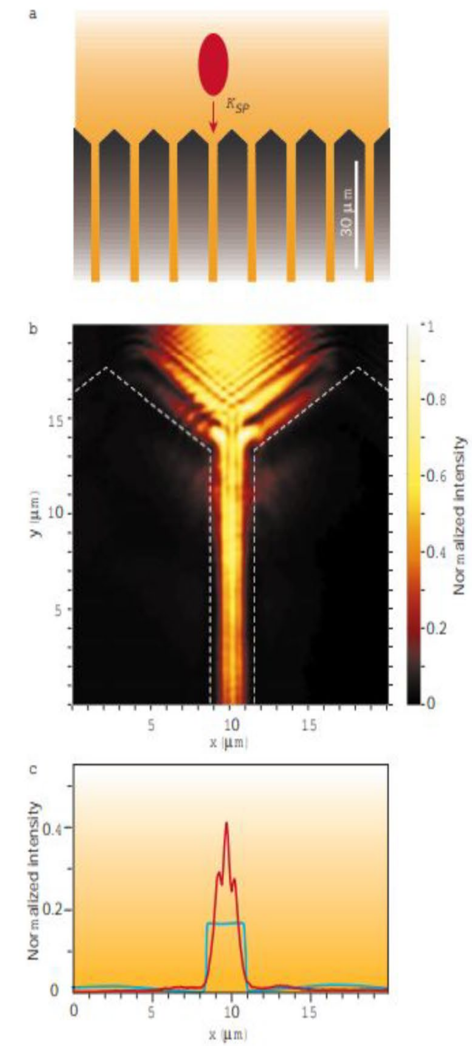
- Rufus Ritchie first observed SPs in the 1950s.
- SPs interaction with surface of a conductor:
  - SPs are light waves that interact with the free electrons on the surface of the conductor. The free electrons oscillate in resonance with the SPs which gives them their unique properties by combining the electromagnetic fields with the electron charge density waves.
- They can confine light at subwavelength scales
  - Potential applications in a wide range of fields including chemistry, physics, biology, and materials science.

Applications and Future Potential

- Enhanced sensing
  - SPs are sensitive to environmental changes
  - Ex: biosensors, chemical sensors
    - Surface-enhanced Raman spectroscopy (SERS): detects a single molecule using SPs
- Optics
  - SPs could be integral for higher resolution microscopes
  - Photonic devices that use SPs
    - Circuits used to propagate SPs can carry electric signals if embedded in dielectric materials
- Smaller components

Applications Cont.

- SPs have led to attempted development of very small photonic circuits, smaller than anything currently used.
  - Due to ability to confine light at nanometer scale
- Figure shows an example in which a 40nm gold stripe is the guide for the SPs.
  - PSTM scan showing SPs bound to metal

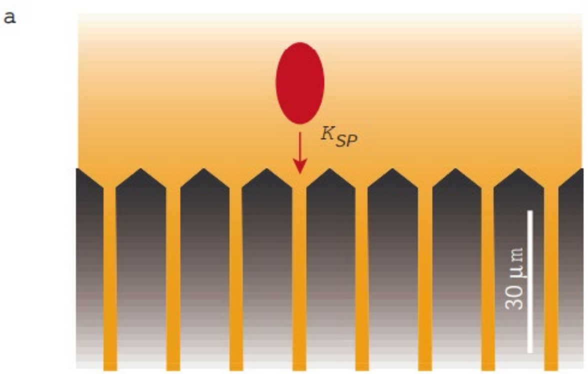


Presented by: Jess Wu

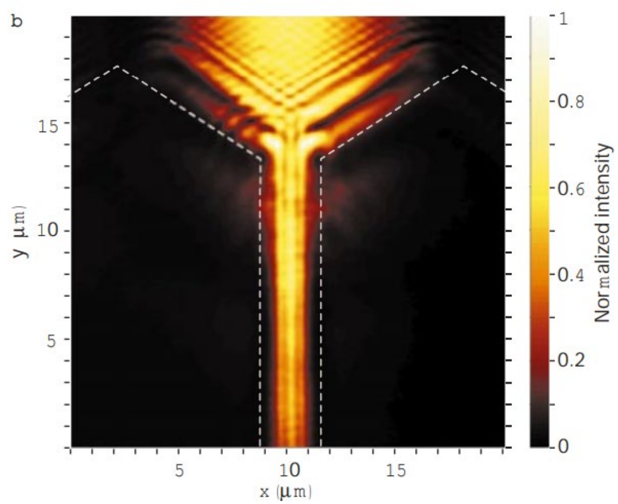
Surface plasmon subwavelength optics

William L. Barnes[1], Alain Dereux[2] & Thomas W. Ebbesen[3]

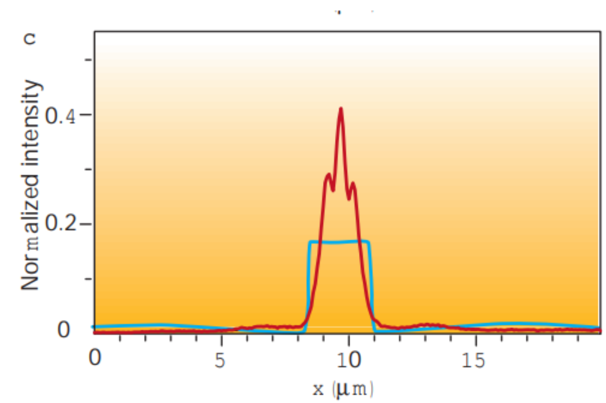
Surface plasmons are waves that propagate along the surface of a conductor. By altering the structure of a metal's surface, the properties of surface plasmons and their interaction with light can be tailored



40nm gold stripe acting as waveguide



Optical functionality of stripe visualized by PSTM



Cross-section across stripe
with AFM topology

Barnes, W., Dereux, A. & Ebbesen, T. Surface plasmon subwavelength optics. *Nature* **424**, 824–830 (2003). https://doi.org/10.1038/nature01937

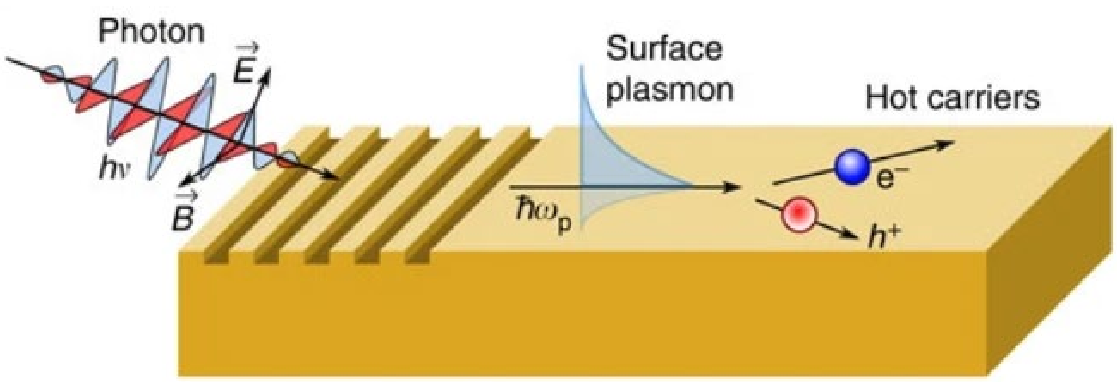
Coupling to surface plasmons

The interaction between the surface charges and the electromagnetic field that constitutes the surface plasmons (SPs) has **two initial consequences:**

1. Momentum of the SP mode > Momentum of free-space photon of same frequency

2. Field perpendicular to the surface decays exponentially with distance from the surface

- Evanescent (near field)
- Consequence of bound, non-radiative SP nature
- Prevents power from propagating away from the surface



Schematic for optical excitation of surface plasmons followed by decay to hot carriers

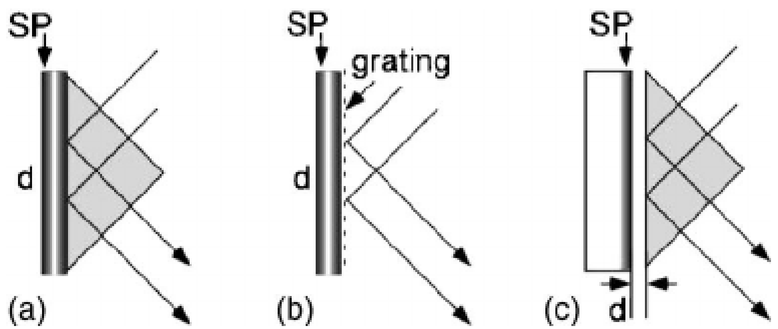
Sundararaman, R., Narang, P., Jermyn, A. *et al.* Theoretical predictions for hot-carrier generation from surface plasmon decay. *Nat Commun* **5**, 5788 (2014). https://doi.org/10.1038/ncomms6788

Current techniques to match momentum:

1. Prism Coupling – enhances momentum of the incident light

2. Scattering from topological surface defect – such as a subwavelength protrusion or hole, generates SPs locally

3. Periodic corrugation in the metal's surface



a. prism coupling b. grating coupling; c. evanescent wave coupling

- Metallic diffraction gratings arise from coupling to SPs. Diffraction (scattering) of light by metallic diffraction grating allows incident light to be momentum match and SP coupled
- Reverse process allows non-radiative SP mode to couple with light

Yury & Vander, R. & Lipson, S.G. & Felsteiner, Joshua. (2006). Visualization of the complex refractive index of a conductor by frustrated total internal reflection. Applied Physics Letters. 89. 021908-021908. 10.1063/1.2220540.

Surface plasmon propagation

Light will propagate once converted into SP mode, but will gradually attenuate due to losses arising from absorption in the metal

propagation length

frequency-dependent permittivity of the dielectric

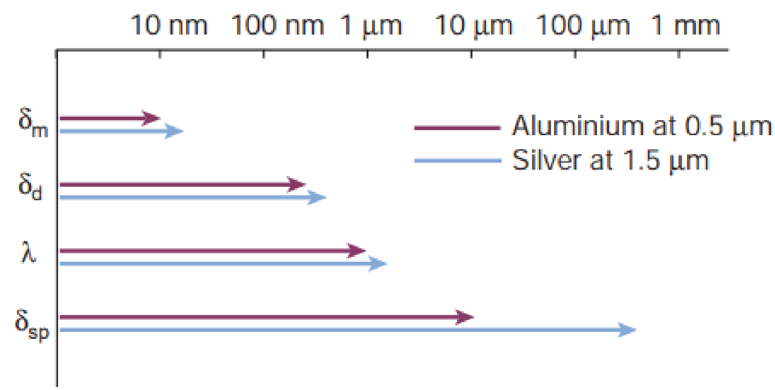
$$\delta_{SP} = \frac{1}{2k''_{SP}} = \frac{c}{\omega}\left(\frac{\varepsilon'_m + \varepsilon_d}{\varepsilon'_m \varepsilon_d}\right)^{\frac{3}{2}} \frac{(\varepsilon'_m)^2}{\varepsilon''_m}$$

Imaginary part of the complex surface plasmon wavevector

$k_{SP} = k'_{SP} + ik''_{SP}$

$\varepsilon_m = \varepsilon'_m + i\varepsilon''$

(frequency-dependent permittivity of the metal)



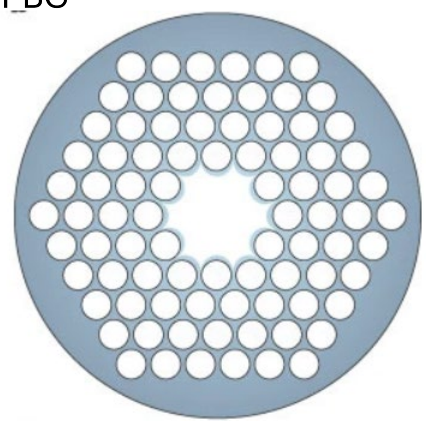
Silver is the metal with the lowest losses in the visible spectrum: propagation distances are typically in the range 10–100 mm, increasing towards 1 mm as one moves into the 1.5 mm near-infrared telecom band

The propagation length sets the upper size limit for any photonic circuit based on SPs

Surface plasmon band structure and periodic surfaces

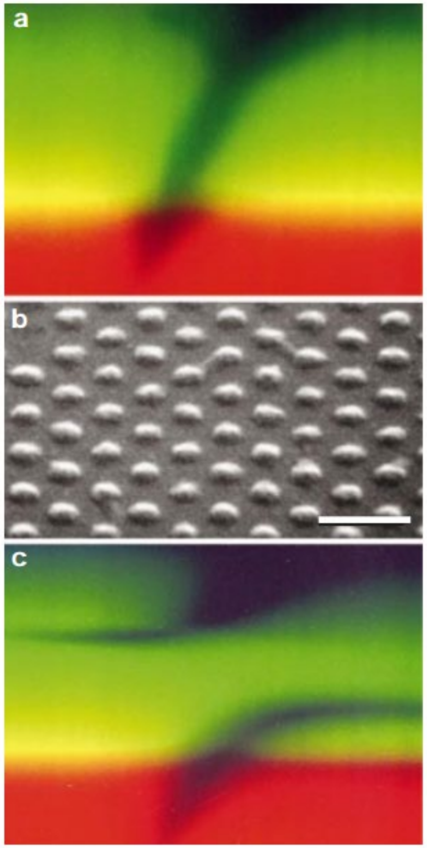
Photonic bandgap (PBG) materials - use wavelength-scale periodic structures to manipulate the interaction between light and matter so as to build new photonic structures

- Using SPs, metals can be used as PBG material in the form of photonic surfaces
- When surface is modulated in both in-plane directions, SP modes may be prevented from travelling in any in-plane direction leading to a full PBG



Photonic crystal fibre – example of PBG, air-guiding fibre in which light is confined to a hollow core by the bandgap of the 2D air–glass photonic crystal cladding

Knight, J. Photonic crystal fibres. *Nature* **424**, 847–851 (2003). https://doi.org/10.1038/nature01940



Limitations & future development of SP technology

- SP device properties are dependent on surface topology & how other SPs are distributed
  - PSTM (microscopy technique) is used to map SP fields
  - PSTM essential for development of SP devices to develop waveguides that direct SP flow
- SP propagation is influenced by the metal type; different metals absorb SPs to different degrees
- Heisenberg uncertainty principle affects measurements of electric/magnetic field
  - $\Delta E \Delta H \geq \hbar c^2 / 2\delta l^4$
    where E and H are electric and magnetic field, δl^4 is the volume in which the electric and magnetic fields are contained

Example of a PSTM microscope; analogous to electron scanning microscope, but uses photons instead of electrons

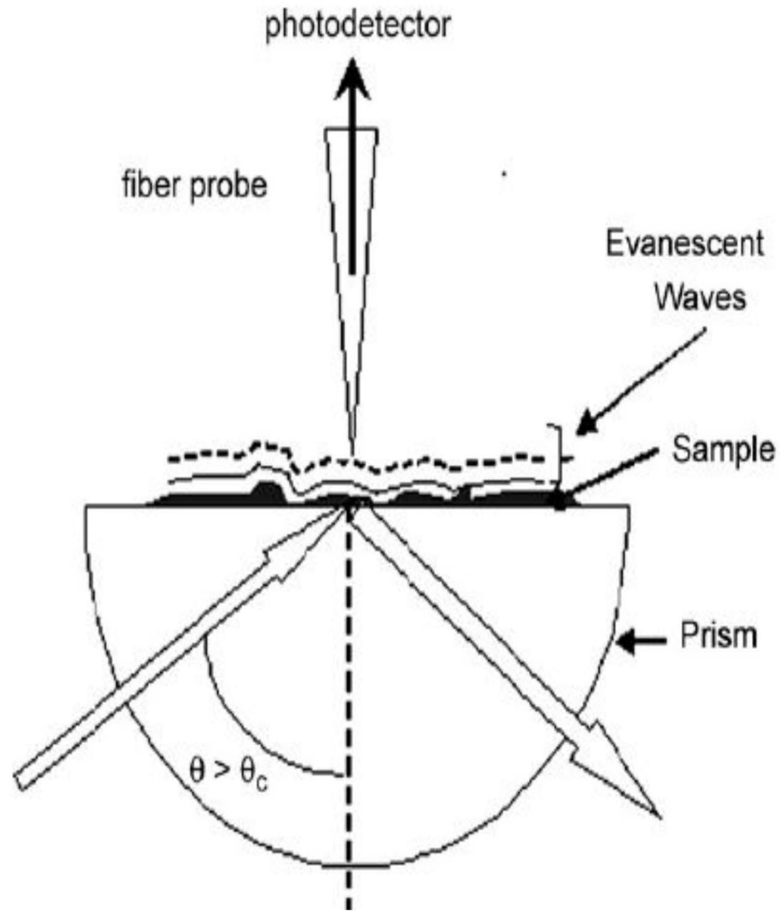
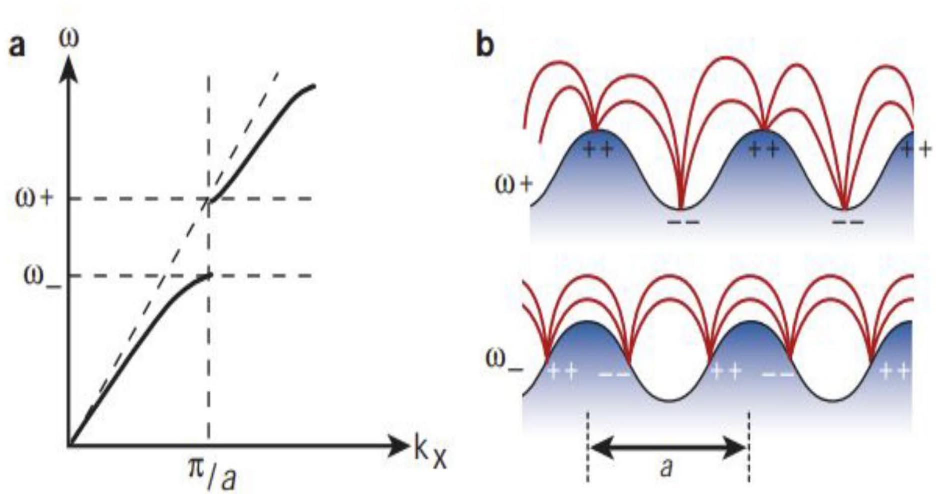


Figure source: https://www.researchgate.net/publication/248280202_Near-field_study_with_a_photon_scanning_tunneling_microscope_Comparison_between_dielectric_nanostructure_and_metallic_nanostructure

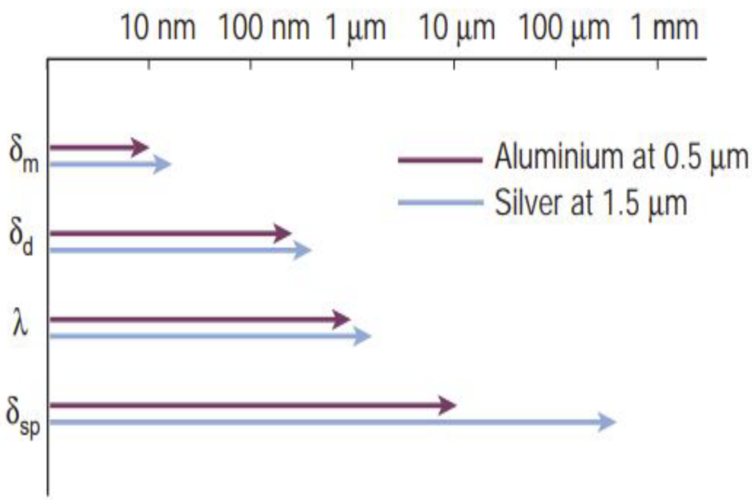
Effects of topology and material properties on SP propagation



Box 3: Example of how surface topology can affect SP device properties; periodic texturing leads to an SP bandgap due to electric field distortion

- Periodic texturing of metal surface with a period equal to half the SP wavelength leads to bandgap formation due to wave interference
- Full SP bandgap can be made by periodically texturing the metal surface in 2 dimensions to block all SP propagation
- At band edges, density of SP states increases significantly, leading to enhanced field

Effects of topology and material properties on SP propagation



Box 2: Example of differing SP propagation depending on SP properties and metal type

- SP device size is limited by propagation length, minimum feature size, decay length in dielectric material & metal
- Propagation length (d_SP) determined by metal loss: 2 mm for aluminum (at 500 nm) and 20 mm for silver (at same wavelength), increasing to around 1 mm at 1.55 µm wavelength
- decay length in dielectric material (δ_d) dictates maximum feature height
- δ_m determines minimum feature size

Waveguides

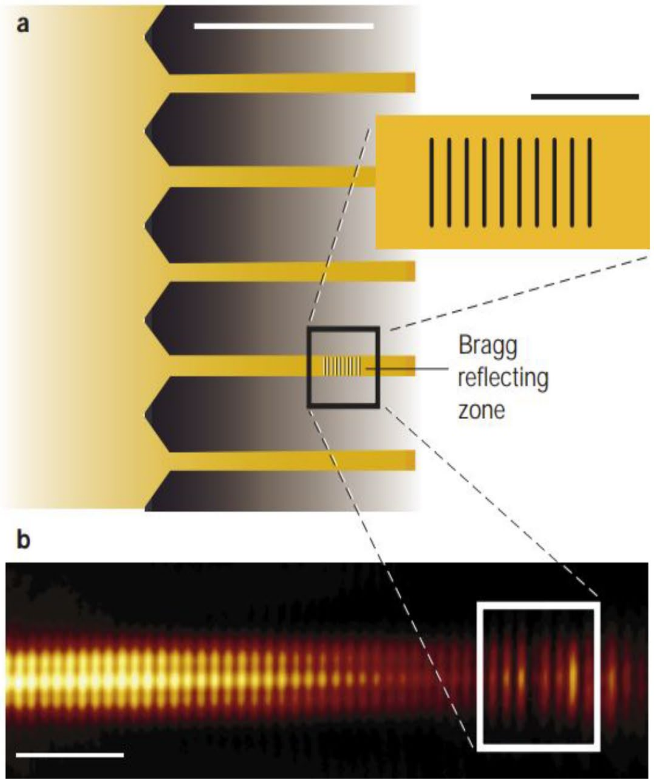


Fig. 3 above shows an example of this texturing

- Different textures of metal surfaces can allow SP to be added to circuits on stripes by changing how it propagates - this is called a waveguide
  - Machine these using lithographic techniques
- Fig. 3 shows a Bragg reflector
  - Part a) shows an example of geometry that can be formed in order to make an SP waveguide; slots are carved in a gold stripe on a glass substrate
  - Reflector creates a mirroring effect from interference between SPs; to the right of the mirror zone the SP intensity drops to the point where SPs are not detected by PSTM

Waveguides

- Waveguides can also be formed by exploiting roughness on a surface to achieve Anderson localization (quantum mechanical effect)
  - This inhibits SP propagation in some direction
  - Form flattened channels on a rough metal film to create this type of waveguide
- Bozhevolnyi et al, 2002
  - Found that SP propagation guiding was most pronounced in 725-785 nm wavelength range, SPs outside the channel were completely dampened while SPs inside were unhindered

http://dx.doi.org/10.1103/PhysRevLett.89.186801

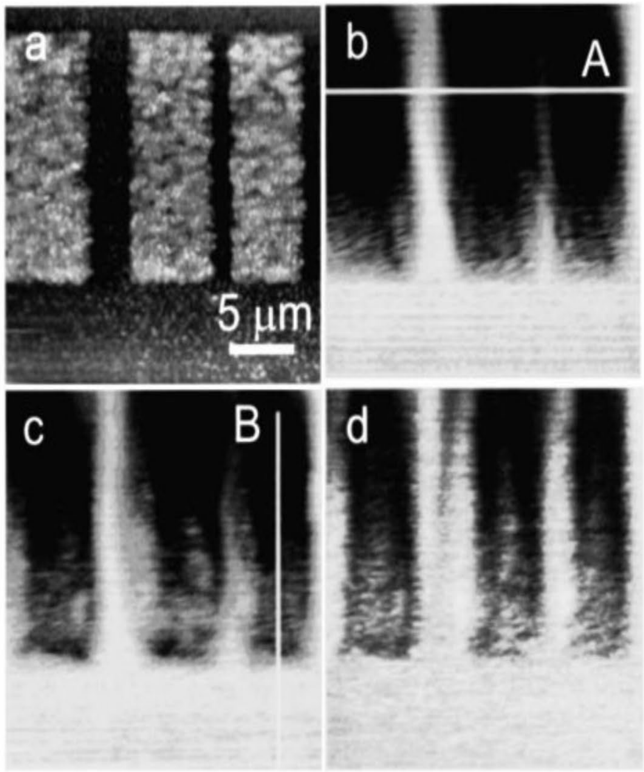


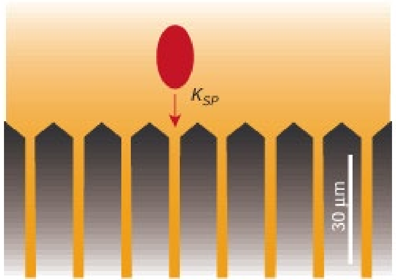
FIG. 2. Gray-scale (a) topographical and near-field optical images ($25 \times 25\ \mu m^2$) taken at $\lambda \cong$ (b) 738, (c) 785, and (d) 833 nm. Regions with random scatterers correspond to the structure shown in Fig. 1(b). Depth of the topographical image is 120 nm.

SP Band Structure

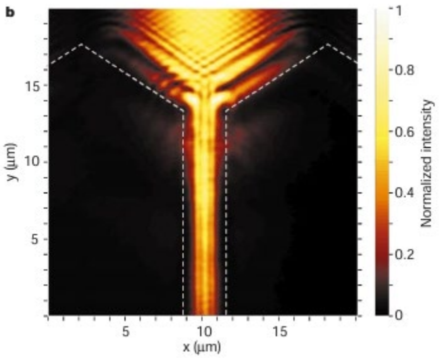
- At frequencies between a band gap the density of SP modes is zero
- At band edges the SP mode dispersion is flat and the density of the SP modes is high
- The frequencies and width of these modes are determined by the particle’s size, material and shape
    - For this they make for good bio-sensing applications
    - And for surface-enhanced Raman spectroscopy (SERS)

Mapping surface plasmons and developing components

- Properties of SP are linked to the activity/distribution of SP on a metal surface
- Much is unknown about the relation between surface topology and SP modes
- Photon scanning tunnelling microscopy (PSTM) used to map the field on metal surface



Micrograph image of gold stripe



PSTM map of the gold Stripe

Mapping surface plasmons Cont…

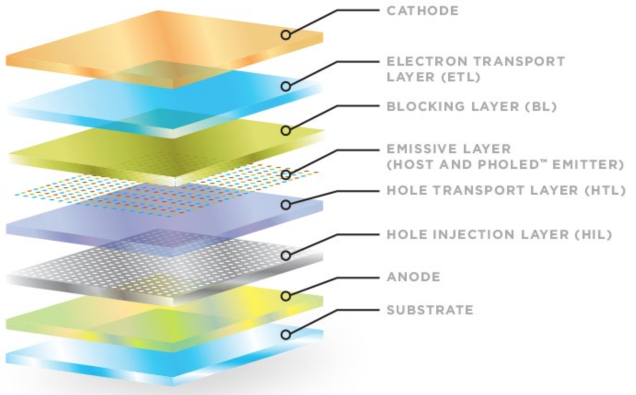
- Enhancing near-field techniques encounters Heisenberg's uncertainty principle

$$\Delta E_i \Delta H_j \geq \hbar c^2 / 2\delta l^4.$$

- Measure the Electric field (E) or Magnetic field (H) with accuracy only when the volume is << than the wavelength of the light in three dimensions
- As volumes smaller than the wavelength are probed, measurements of optical energy become uncertain, highlighting the difficulty with performing measurements in this regime.

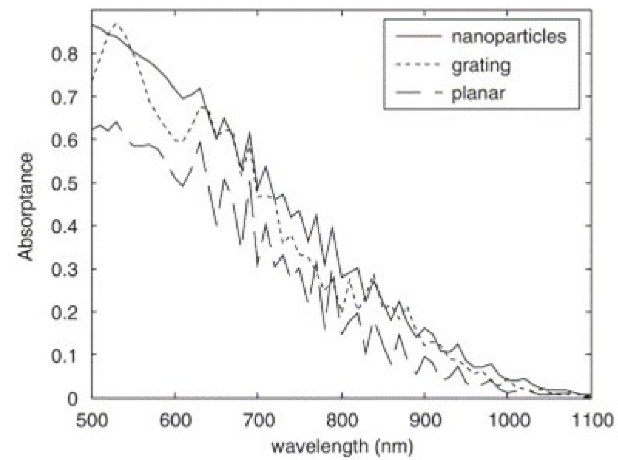
Future Directions

- Surface Plasmons are being studied further for their ability to generate light
  - Example include that of an organic light-emitting diode (OLED)
- In OLEDs, excitons are produced by charging a semi-conducting organic layer, which is about 100 nm thick.
- The proximity of excitons to the metallic cathode, which injects electrons, leads to a significant loss of power to SP modes on the cathode surface, reducing device efficiency.
- To enhance device efficiency, especially for high-efficiency, long-life, and full-colour devices, managing or recovering lost power through a periodic nanostructure is crucial.



Future Directions Cont…

- In addition to maximizing efficiency to produce light, the opposite is being studied in order to absorb light and generate power
    - Example would be in the use of SP in solar cells
- A 2006 study was published which concluded that absorption enhancement is possible by using SP excitations on metallic nanoparticles more so with smaller wavelengths, but effective absorption with larger wavelengths is possible



Catchpole, K. R., & Pillai, S. (2006). Surface plasmons for enhanced silicon light-emitting diodes and solar cells. *Journal of Luminescence*, *121*(2), 315-318.

Future Directions Cont…

- To develop SP-based photonics, non-linear components such as switches will also be required
- Only recently have experiments been designed to look further into how non-linear effects may be used to discover new elements of SP-based photonics
- SP’s are introducing a new class of subwavelength photonic devices
- Nano-scale lithography has already helped scientists develop proof of concepts to new applications for SP’s
    - Wave guides, Reflectors, Beam splitters,Enhanced transmission, Beaming
- The goal of making a completely plasmonic circuit still requires much more research

Synthesis and Applications of Graphene in MEMS-based Systems

Liwei Lin
Professor, Mechanical Engineering Department
Co-Director, Berkeley Sensor and Actuator Center
University of California at Berkeley

Berkeley
UNIVERSITY OF CALIFORNIA

Outline

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

→What are the special characteristics?

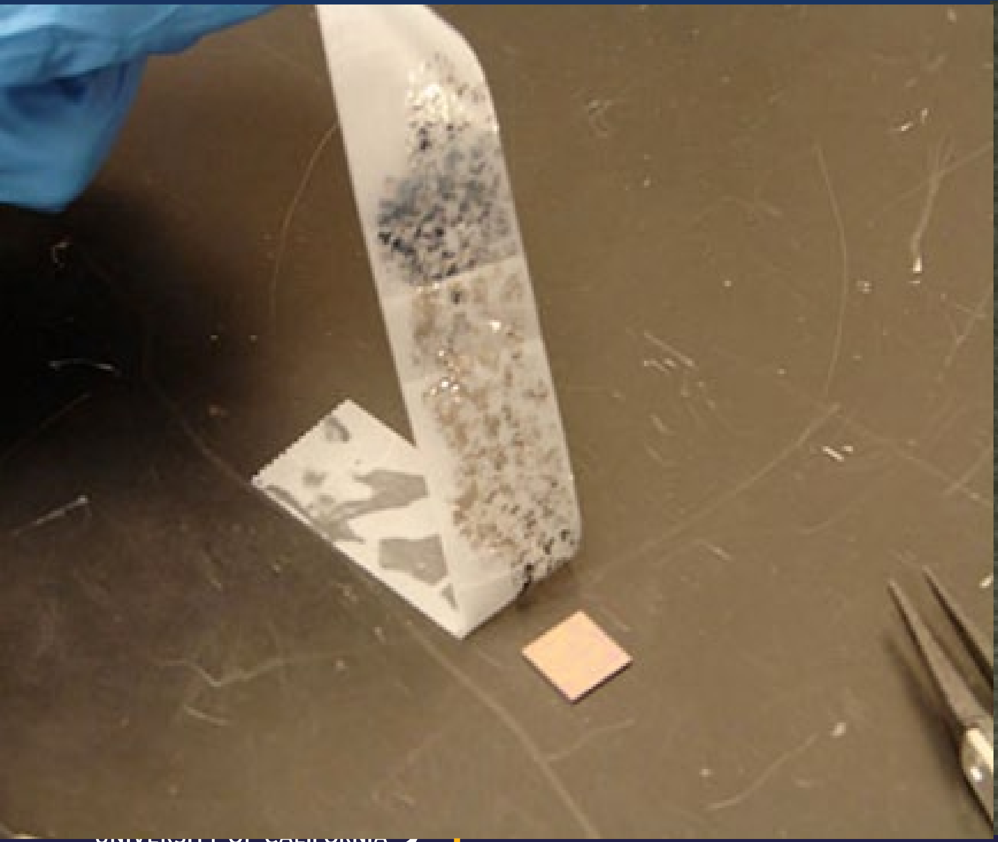
→Does it work?

→Can it improve the graphene production?

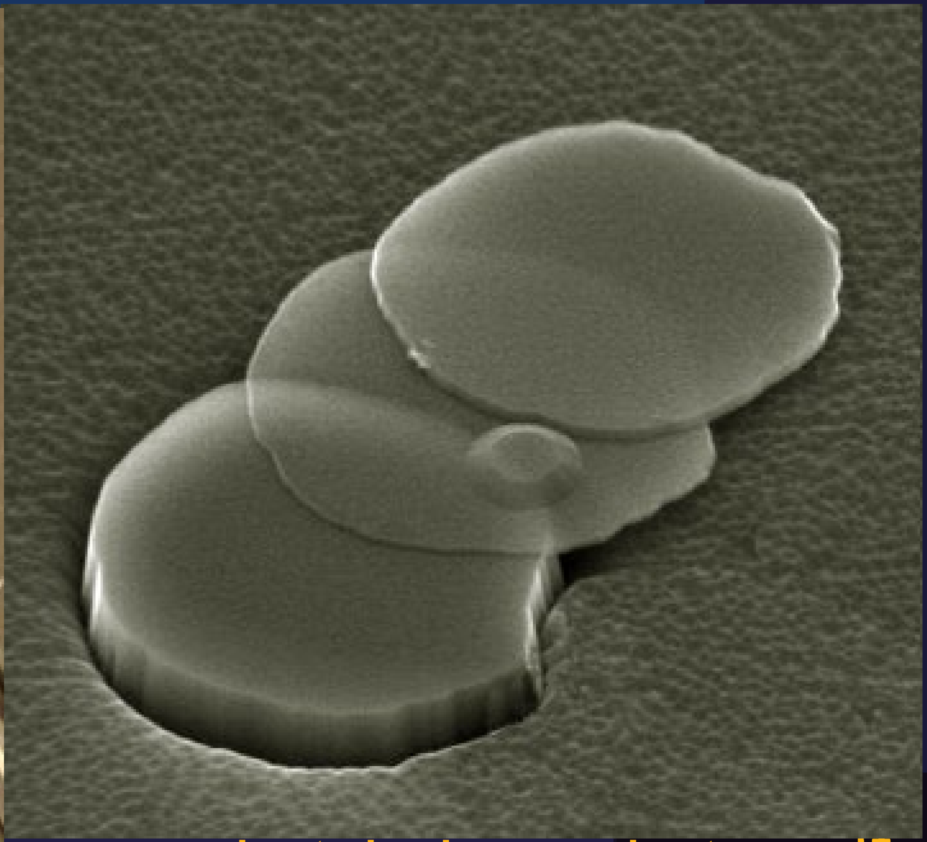
- **Flexible gas sensors based on graphene FETs**
  - **Flexible substrate, graphene FETs, sensing characterizations …**
- **Graphene-on-diamond thin film UV detector**
  - **Concept, fabrication, sensor testing results …**

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



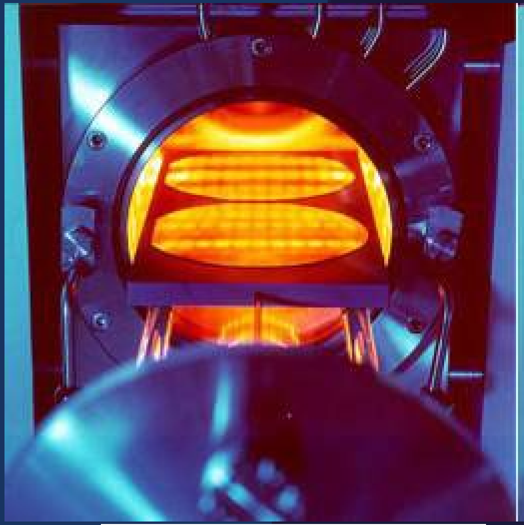
www.sciam.com



www.condmat.physics.manchester.ac.uk

MEMS for High Cooling Rate?

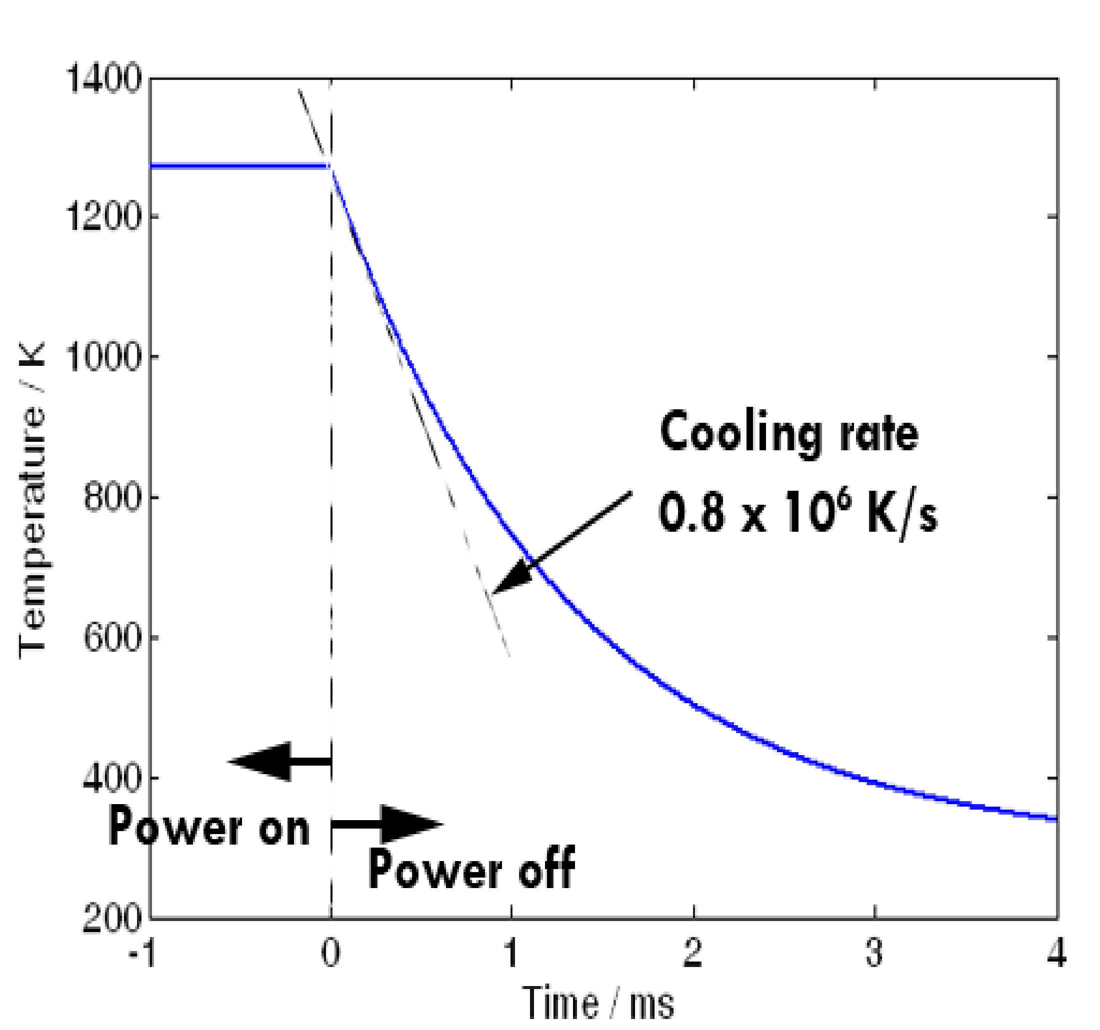
- **Several minutes to several hours** for a common CVD system to cool down
- By abruptly exposing CVD chamber to outside environment or by flowing cold gas into the chamber at a high rate, time constant can be reduced to **~10 seconds**
- It is difficult to further reduce thermal time constant because 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 Chemical Vapor Deposition," *IEEE/ASME Journal of Microelectromechanical Systems*, Vol. 20, pp. 9-11, 2011

Cooling Rate in μCVD

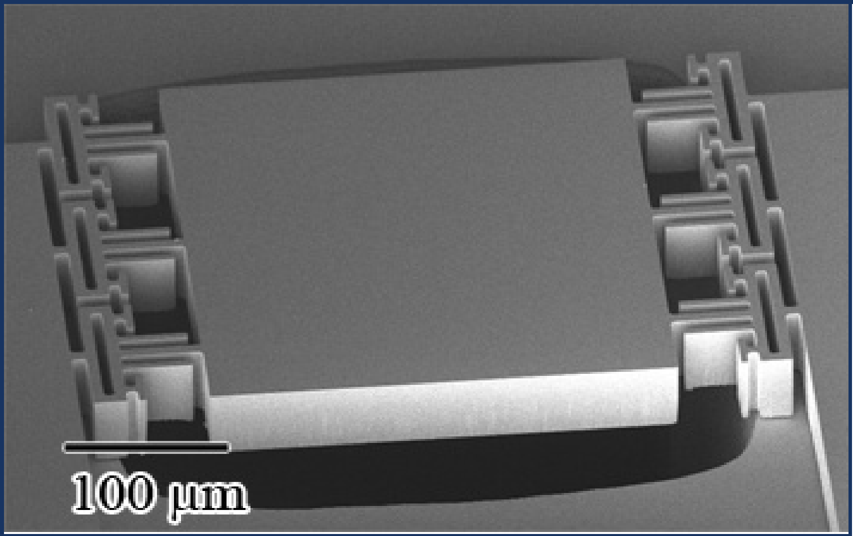
- The heat capacity C_h of the system scales with volume or L^3
- The heat resistance R_h, on the other hand, scales with L^{-1}
- the time constant of the system $\tau_h = R_h C_h$ should scale with L^2
- CVD system from macro (0.1~1m) down to micro (~ 300μm) ➔ ~10^{-6} reduction of time

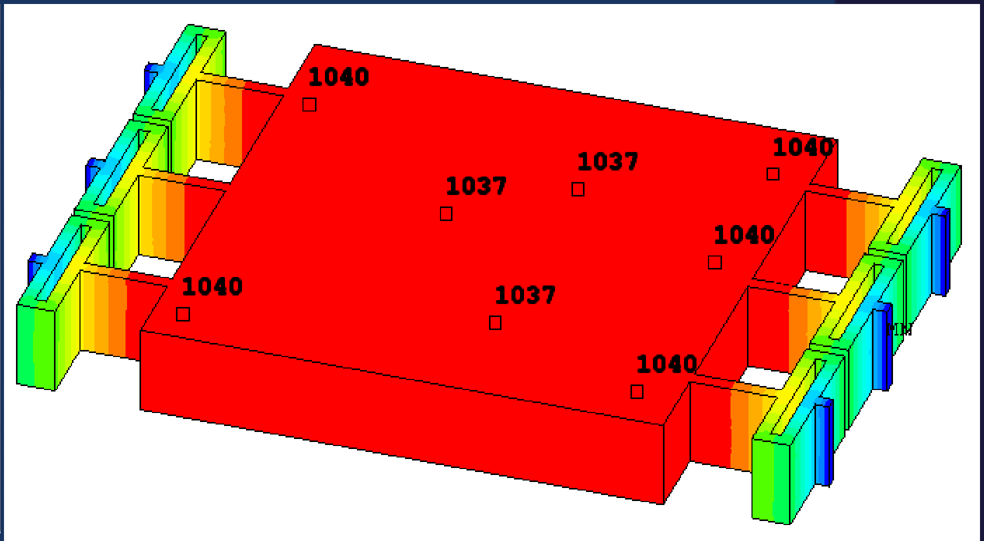


- Time constant from ~ 10 mins down to ~ one millisecond!!

Berkeley
UNIVERSITY OF CALIFORNIA

μ-CVD MEMS Structure Design



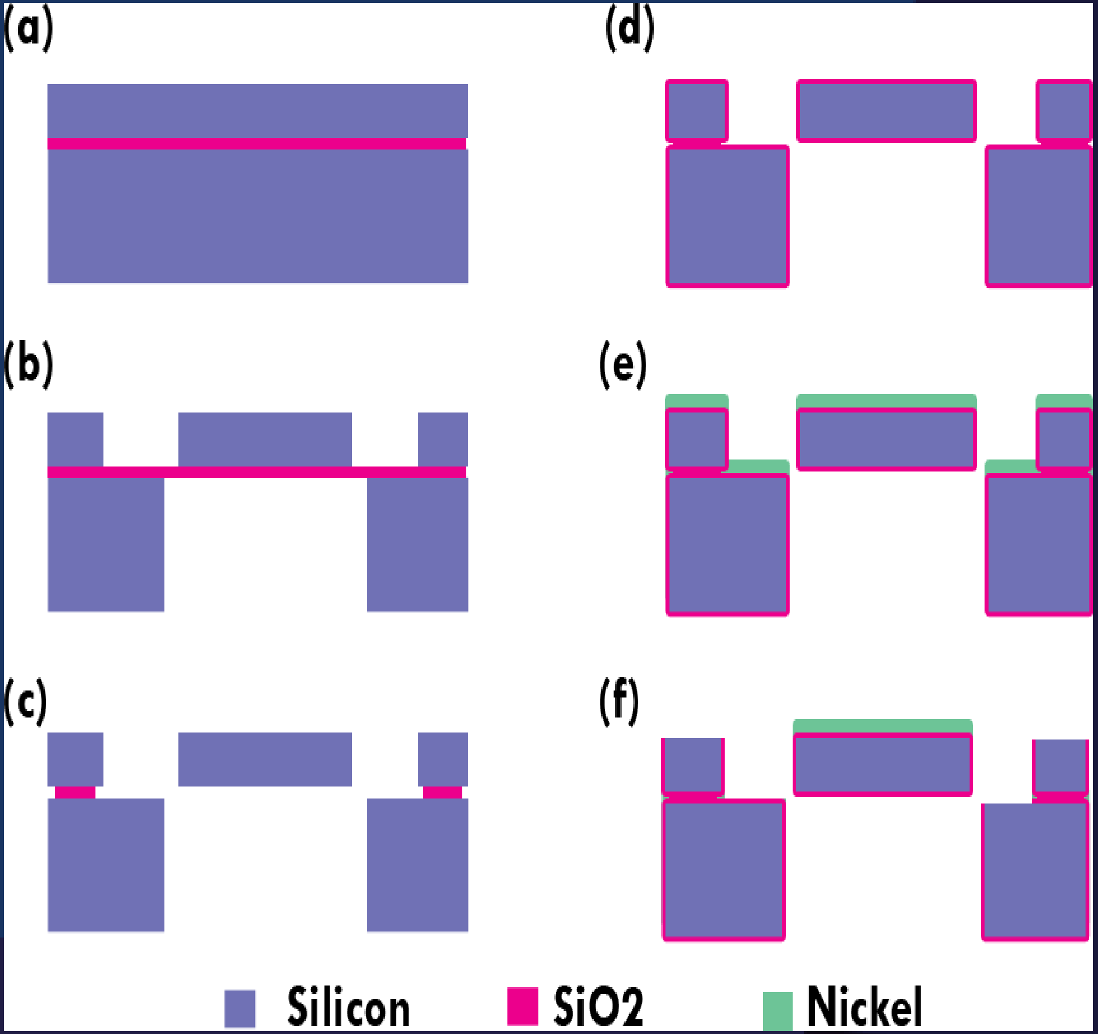


- Folded beams to release thermal strain on the platform
- ANSYS® analysis shows a heating stage at 1000ºC with temperature variations within 5ºC
- Uniform temperature field is critical for nickel to absorb carbon for consistent number of graphene layers

Berkeley
UNIVERSITY OF CALIFORNIA

Device Fabrication

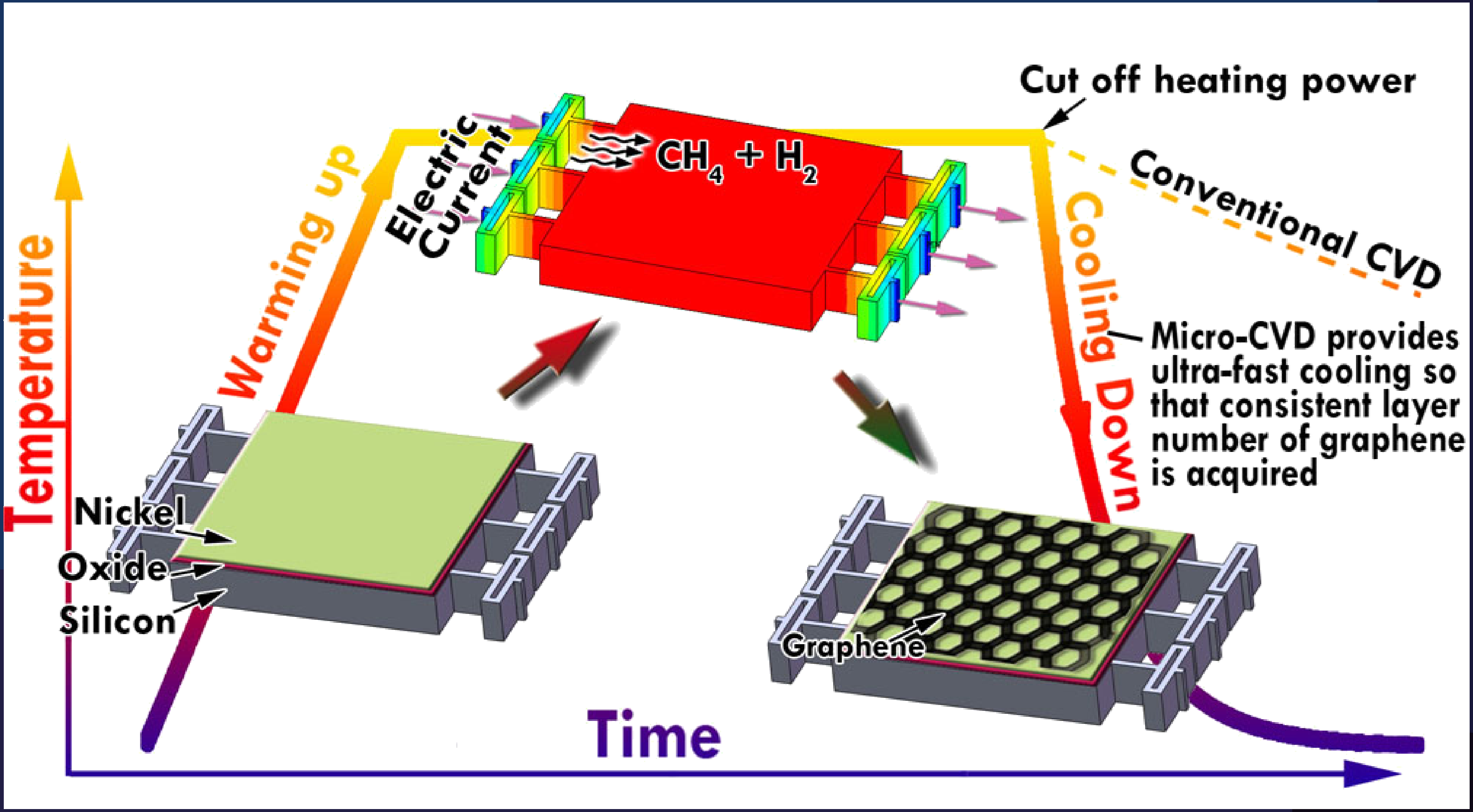
- (a) SOI wafer.
- (b) Back-side opening and front side etch for heating stage
- (c) Structure release in buffered HF solution.
- (d) Thermal oxidation to grow 150nm SiO2
- (e) Evaporate 300nm thick nickel layer.
- (f) Etch away nickel and SiO2 on anchors.



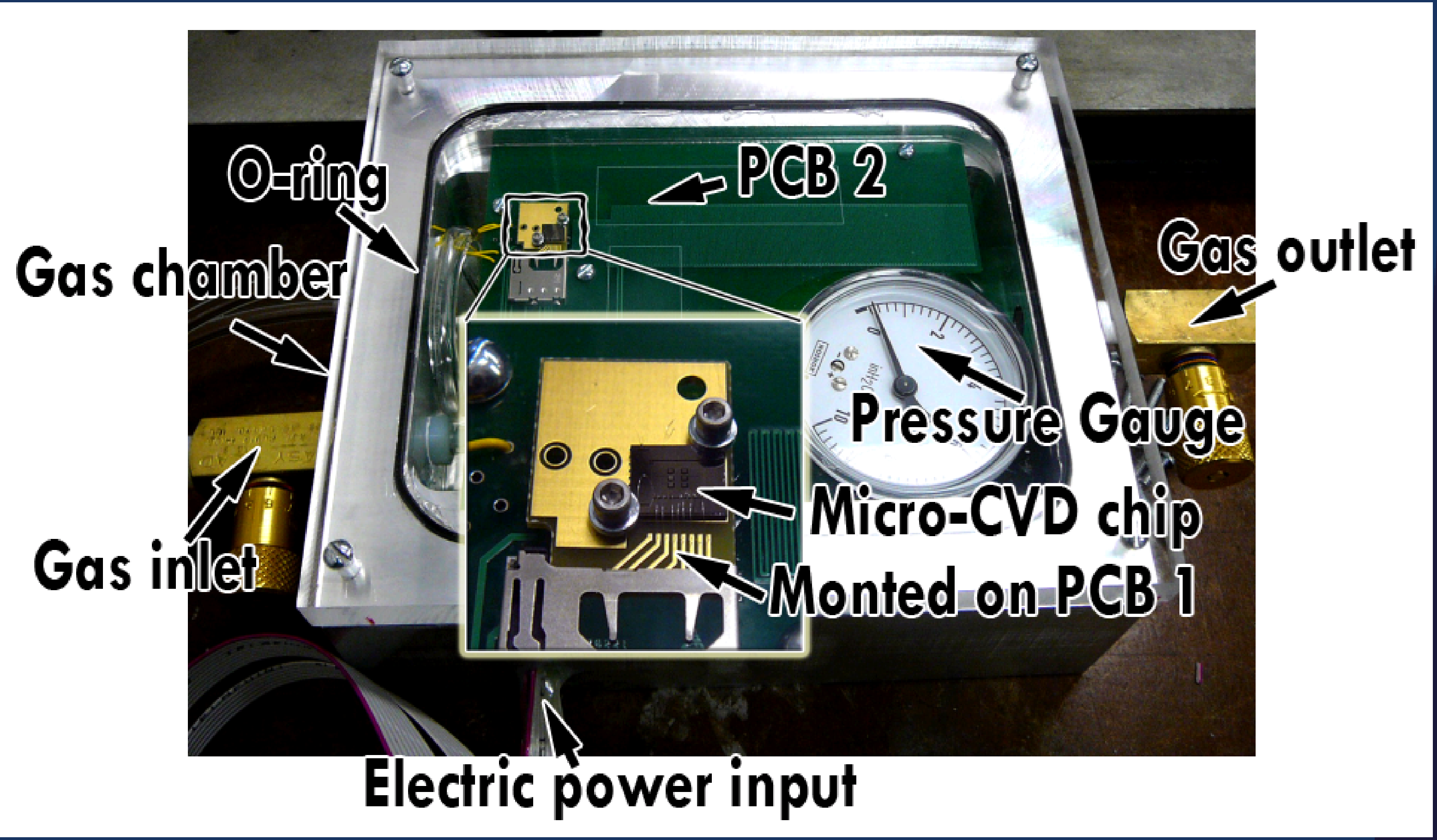
Berkeley
UNIVERSITY OF CALIFORNIA

Graphene Synthesis by μ-CVD

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



Experimental Setup

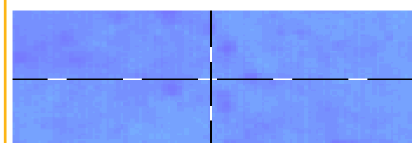
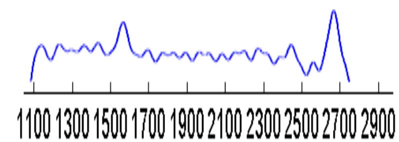
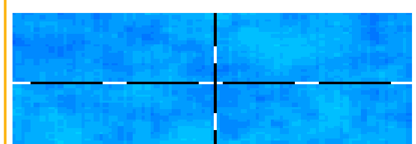
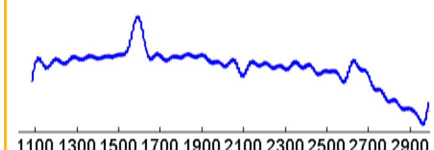
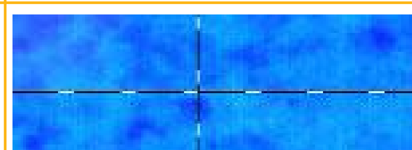
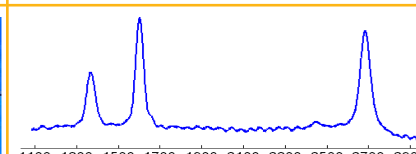
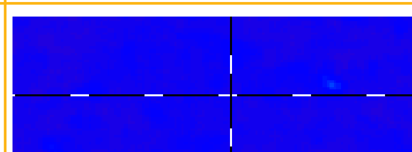
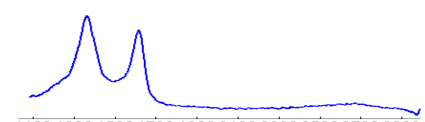


- μ-CVD chip is mounted on a printed circuit board for gas and electrical interface

Berkeley
UNIVERSITY OF CALIFORNIA

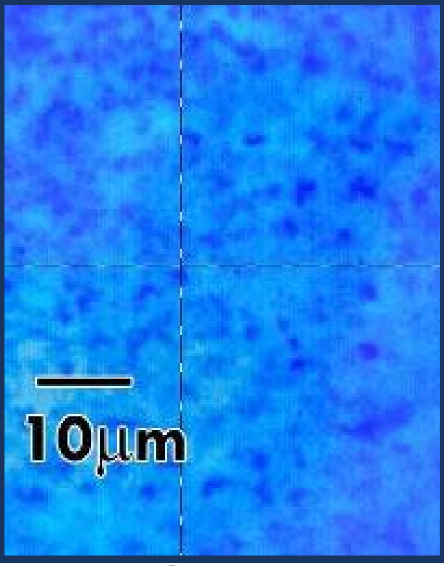
Experimental Results

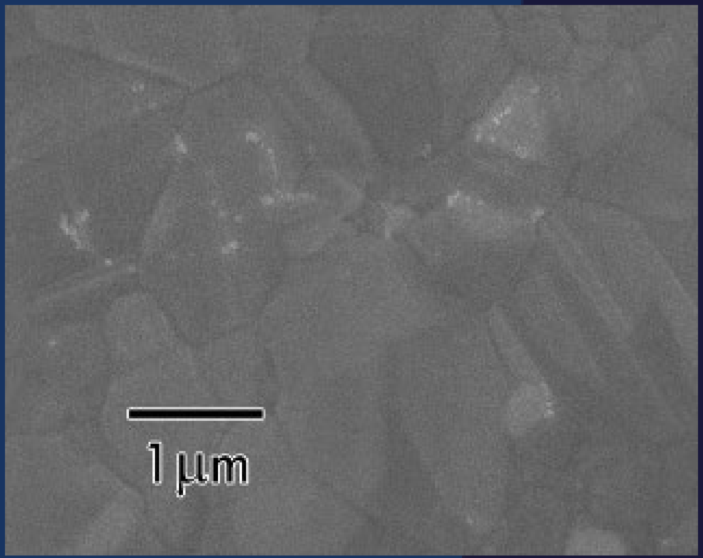
- Joule heating produced an estimated temperature of **1000 ºC** in hydrogen environment. **Methane** is introduced as the carbon source for **5 mins**

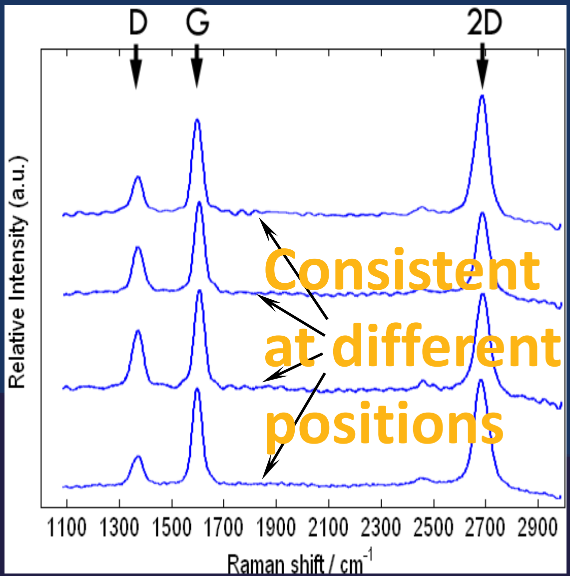
Power (mW)	Result	Optical Image	Raman Spectra	Success?
220	No material detected			No
250	dots could be seen			No
280	**Scattered dots with darker color**			**Yes**
310	Very dark			No
350	Supporting beams failed after few seconds heating			No

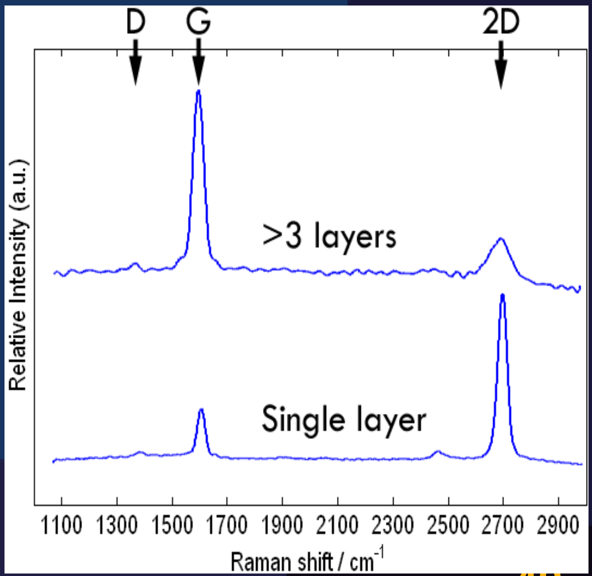
Results and Analyses

- 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





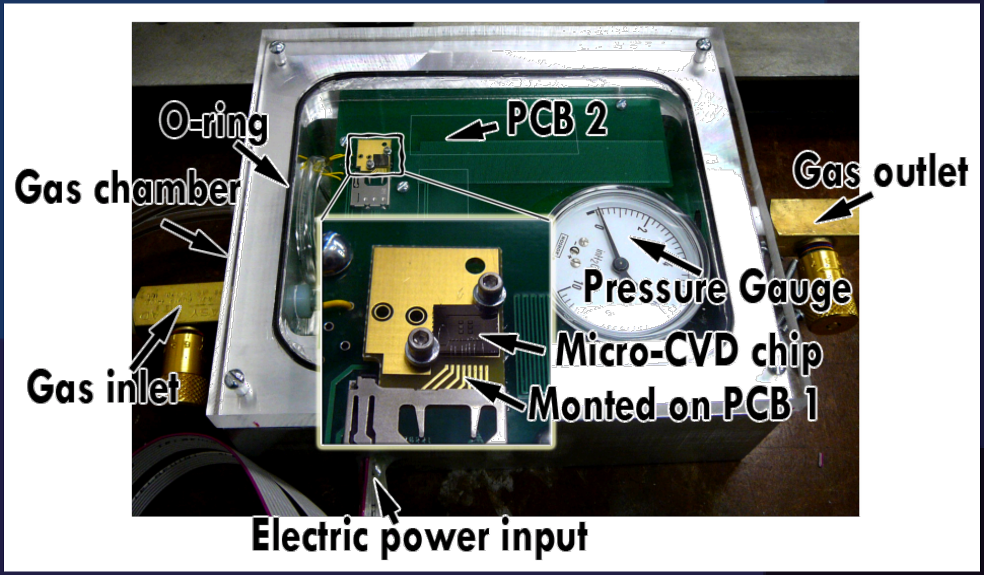




Berkeley
UNIVERSITY OF CALIFORNIA

Short Summary

- Uniform bi-layer graphene synthesis in the miniaturized CVD platform of 300×300μm^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.



Berkeley
UNIVERSITY OF CALIFORNIA

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 …

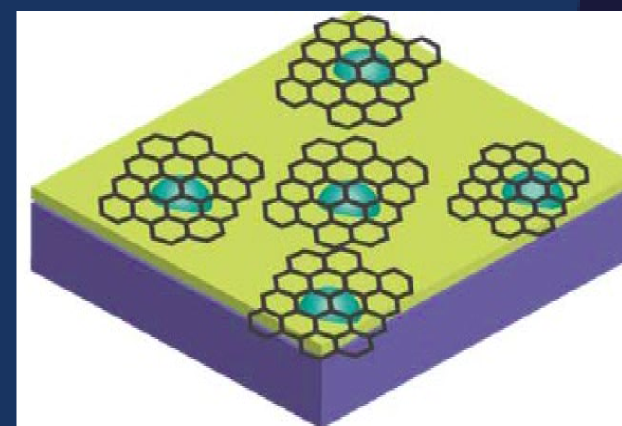
Berkeley
UNIVERSITY OF CALIFORNIA

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?**

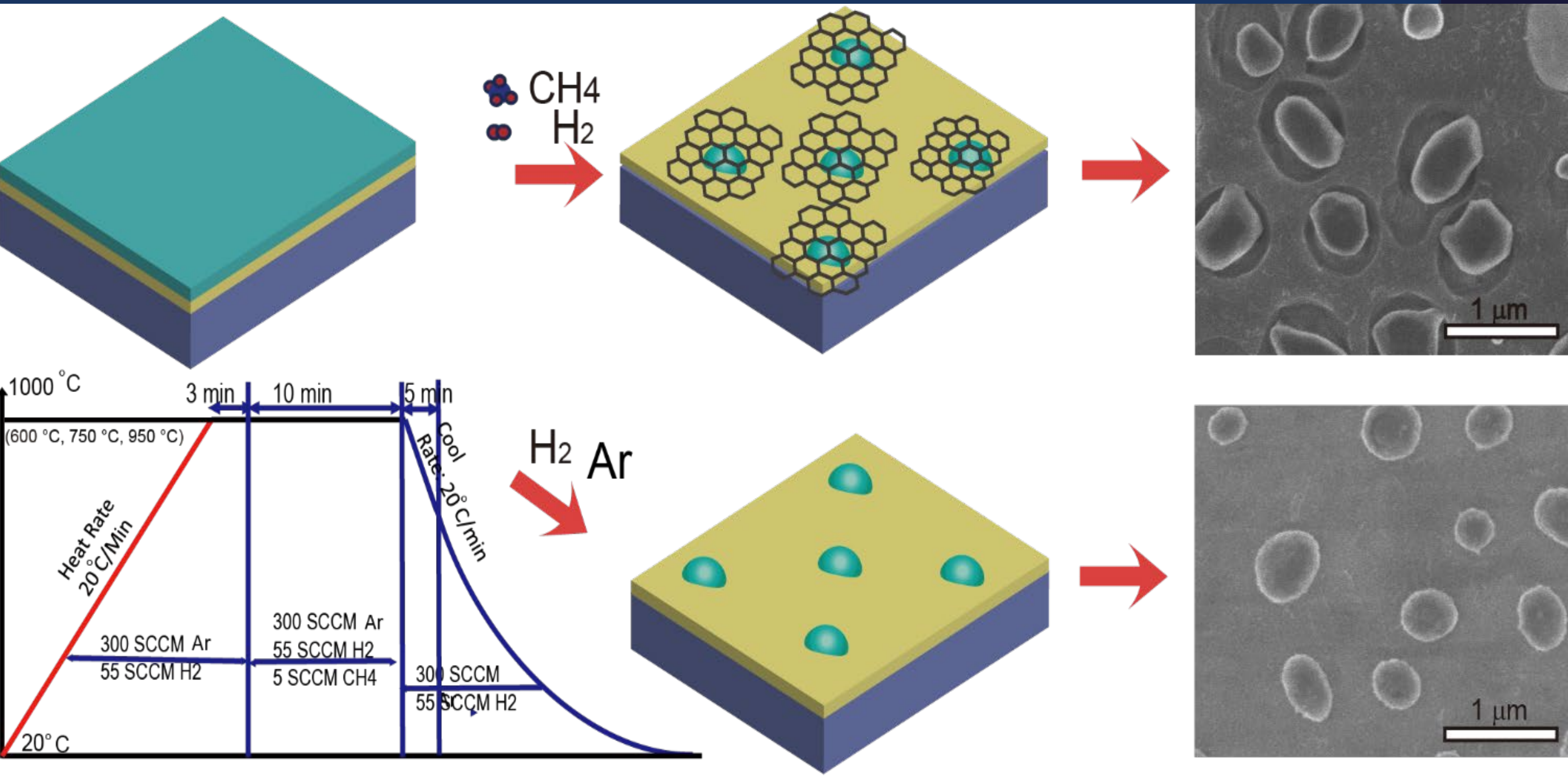
Synthesis by a Single Droplet

?



Synthesis by Multiple Droplets

Large Area via Multiple Droplets?



Scattered graphene of hexagonal tents cover the metal droplets

Berkeley
UNIVERSITY OF CALIFORNIA