

# Crucial role of Nanomaterial Development for Nanocharacterization



**Annop Klamchuen**

**Nano Characterization Laboratory (NCL)  
National Nanotechnology Center (NANOTECH), Thailand**



# ABOUT US....





# MOST

Ministry of Science and Technology of Thailand

NSTDA BOARD

NSTDA

**BIOTEC**  
a member of NSTDA

National Center Genetic Engineering and Biotechnology

**NECTEC**  
a member of NSTDA

National Electronics and Computer Technology Center

**MTEC**  
a member of NSTDA

National Metal and Materials Technology Center

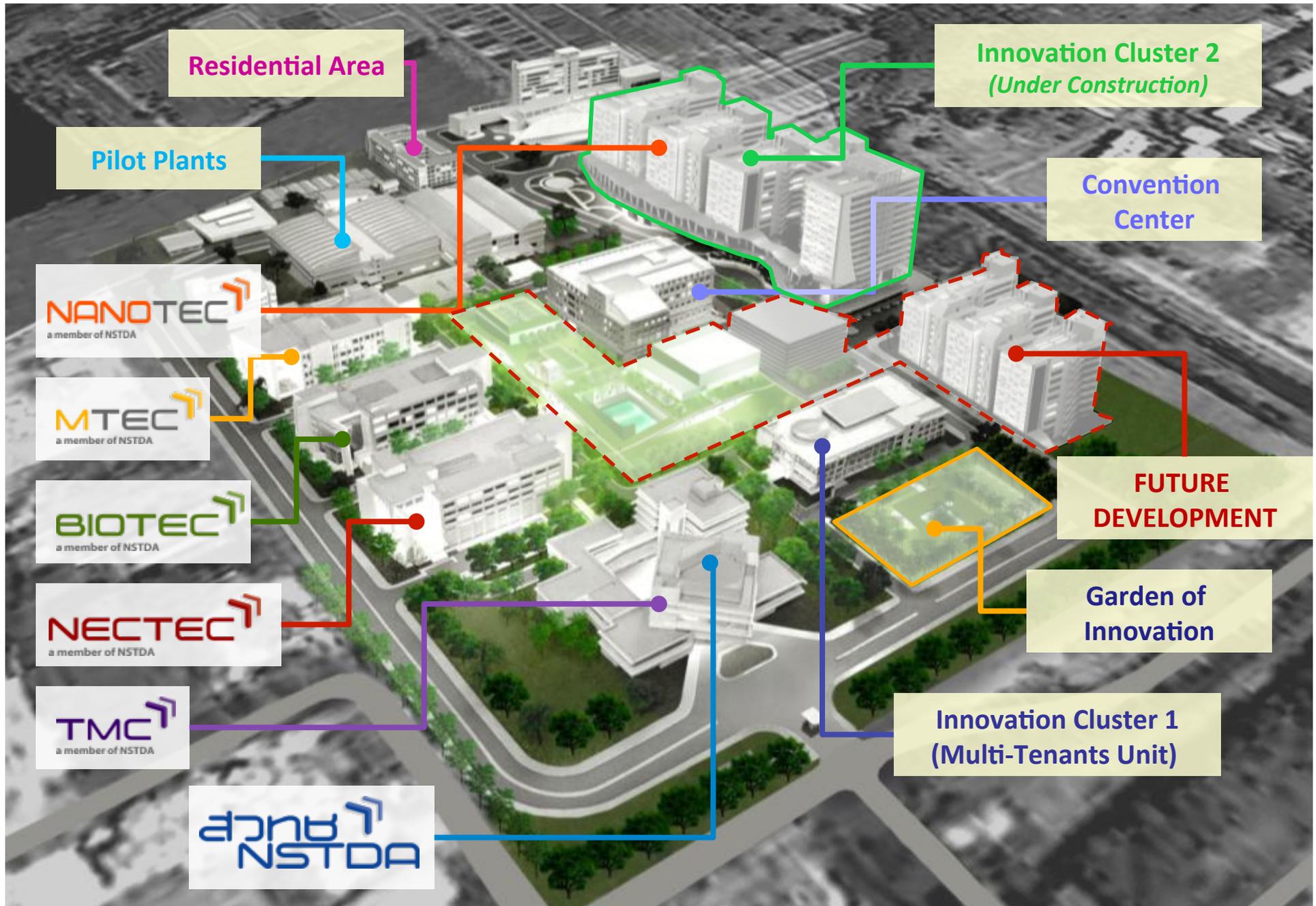
**NANOTEC**  
a member of NSTDA

National Nanotechnology Center

**TMC**  
a member of NSTDA

Technology Management Centre

# S&T Community in TSP





Prof. Sirirurg Songsivilai, M.D., Ph.D.  
Executive Director

**NANOTEC** is an internationally-recognized Nanotechnology Center, conducting R&D programs that have major impacts on the development of Thailand

### **Our Direction:**

- High Impact Program **(National Importance)**
- World-class R&D **(International Excellence)**
- International Player **(Global Visibility)**

# NANOTEC Research Center



*Dr. Chalong Laochariyakul*  
Deputy Executive Director



NLH

*Dr. Uracha Ruktanonchai*  
Research Unit Director

Nanotechnology for Life  
& Health Science  
Research Unit

Nano Delivery  
System (NDS)

Nano Molecular  
Target Discovery  
(TDI)

Nano  
Cosmeceutical  
(NCM)



NSM

*Dr. Wiyong Kangwansupamonkon*  
Research Unit Director

Nanostructure &  
Nanometrology  
Research Unit

Nano  
Characterization  
(NCL)

Nano Safety & Risk  
Assessment (SRA)

Nano Agro & Food  
Innovation (NAF)

Hybrid Nanostructure  
& Nanocomposites  
(HNN)



MAT

*Dr. Kajornsak Faungnawakij*  
Research Unit Director

Nanomaterials &  
Nanosystems Engineering  
Research Unit

Nanomaterial for  
Energy & Catalysis  
(NEC)

Integrated Nano  
System (INS)

Nano Scale  
Simulation (SIM)

Nanoengineered Soft  
Materials for Green  
Environment (SOF)



FUN

*Dr. Udom Asawapirom*  
Research Unit Director

Functional  
Nanomaterials &  
Assembly Research Unit

Functional  
Nanomaterial &  
Interfaces (FNI)

Engineering &  
Manufacturing (ENM)

Nanostructure &  
Functional Assembly  
(NFA)

Nano Functional  
Textile (NFT)

# Crucial role of Nanomaterial Development for Nanocharacterization



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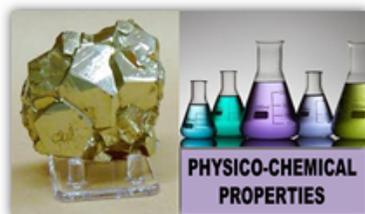
# LACK OF INFORMATION



REAL or FAKE ?

REAL with QUALITY ?

REAL with SAFETY ?



## INFORMATION OF THE TEST ITEM (CLOSED TO) CORRECT ONES

- WHICH PART IS CLAIMED NANO ?
- COMPOSITION OF THE NANO
- FUNCTION CLAIMED



# Characterization & Regulatory Gaps of Nano Products

- No agreed protocols for physico-chemical characterization
- Existing 'methods of test' may not be suitable for nanoscale devices and dimensions
- Measurement techniques and instruments need to be developed and/or standardized
- Calibration procedures and CRMs needed for validation of test instruments at nanoscale

The screenshot shows the NPR website interface. The main article is titled "Safety of Nano-Cosmetics Questioned" by Nell Greenfeldboyce, dated March 13, 2006. The text discusses Andrew Maynard's role as a science advisor for the Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars. It mentions that the center has launched a new website with a searchable list of 212 commercially available nano-products, primarily cosmetics. A small image of various cosmetic products is visible at the bottom left of the article.

The screenshot shows the BBC News website. The main article is titled "Toxic warnings for nano industry" by Jonathan Fildes, dated Thursday, 4 May 2006. The article discusses the Royal Society of the UK's warning that the nano industry should disclose how it tests products containing nanoparticles. A small image of carbon nanotubes is shown at the bottom right of the article.

The screenshot shows the FDA website. The main article is titled "FDA Continues Dialogue on 'Nano' Regulation". The article discusses the FDA's ongoing dialogue with industry and academia regarding the regulation of nanotechnology. It mentions that the FDA is working with the White House, the National Nanotechnology Initiative, and other U.S. government agencies to develop a regulatory framework for nanotechnology. A small image of a molecular structure is shown at the bottom right of the article.

# Nanotechnology Value Chain

**Nanomaterials**

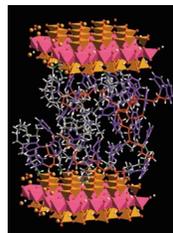
**Nanointermediates**

**Nano-enable products**

**Nanoscale structures in unprocessed form**

**Intermediate products with nanoscale features**

**Finished goods incorporating nanotechnology**



***Needs !!***

**Test methods, Instruments, Standards, Safety**

**Nanotechnology may become  
a new non-tariff barrier !!!**

# Technology Roadmap of NCL

NCL has focused its research and measurement service activities on nanoscale physico-chemical **characterization and standardization**

## National Advanced Nano-characterization Center (NANC)

Nano Imaging Laboratory



Advanced Optical Microscopy & Spectroscopy Laboratory



Nanoparticle Detection & Sizing Laboratory



Integrated NanoMaterials Characterization Laboratory



Analytical NanoChemistry Laboratory



NanoProduct Functionality & Specification Laboratory



Nanoproduct safety Laboratory



Flagship program



Targeted Nanoproducts

- Cosmetics
- Food
- Petrochemicals



Product labeling

# Our Research & Development Focus

“Measurement method/test development for Nanocharacterization”

Material fabrication & Design

R & D

Sample Preparation method for Characterization

Characterization technique improvement

“Raman spectroscopy”

**Sample Preparation and Physico-Chemical Characterization of Nano-Products**

Sample: Nanomaterials (NM) in a complex matrix (Inhomogeneous, complex, and vary concentrations e.g. Metal-oxide NM in samcones)

**Morphology & Composition**

(1) Sample Preparation Methods for Morphology and Composition — SEM/EDS

Viscosity measurement

Low viscosity → High viscosity

Blade-coated deposition → Spin-coated deposition

Thin film

Detection and Characterization of nanomaterials by SEM and EDS

**Sample Preparation and Physico-Chemical Characterization of Nano-Products**

Sample: Nanomaterials (NM) in a complex matrix (Inhomogeneous, complex, and vary concentrations e.g. Metal-oxide NM in samcones)

(II) Sample Preparation Methods for Particle Size — DLS (ISO 22412)

a) Sample pretreatment — Homogenization

b) NM enrichment — Centrifugation

c) Stabilization of NM suspension

- Dilution
- Dilution agent
- Sonication

Characterization of nanoparticle size distribution by DLS

Series	nm	Intensity	Volume	Number
1	121.103	98	1	1
2	393.632	20	1	1
3	381.113	99	1	1
4	381.012	98	1	1
5	182.612	99	1	1
6	381.012	98	1	1

**การพัฒนาเทคนิควิเคราะห์สารอินทรีย์และอนินทรีย์ในตัวอย่างที่ซับซ้อนด้วย Inductively Coupled Plasma Mass Spectrometry**

ขั้นตอนการวิเคราะห์: การเตรียมตัวอย่าง → การวัดสัญญาณ → การวิเคราะห์ข้อมูล

เทคนิคการวิเคราะห์: TOGA, ICP-MS

การวิเคราะห์เชิงปริมาณ: การสร้างมาตรฐาน → การวัดสัญญาณ → การคำนวณความเข้มข้น

“This patent: 1003001786”

**ชุดวิธีการเตรียมตัวอย่างของสารประกอบอินทรีย์และอนินทรีย์ในตัวอย่างที่ซับซ้อนด้วย degassing แบบลดปริมาณโดยใช้ของเหลวแห้งได้ เพื่อการวิเคราะห์ด้วยเครื่องวัดสเปกตรัมมวลแบบ Inductively Coupled Plasma Mass Spectrometry**

ขั้นตอนการเตรียมตัวอย่าง: การเตรียมตัวอย่าง → การวัดสัญญาณ → การวิเคราะห์ข้อมูล

เทคนิคการวิเคราะห์: degassing แบบลดปริมาณโดยใช้ของเหลวแห้งได้

“This patent: 100300200”

**Texture Orientation of Ag Thin films grown via Gas-Timing RF Magnetron Sputtering**

NSTDA U.S. Patent

“This patent: 1001005550”

**Crucial Role of Reactive Pulse-Gas on Sputtered Zn3N2 Thin Film Formation**

Reaction mechanism: Zn + N2 + H2O → Zn3N2 + H2

Effect of pulse gas: Pulse gas (H2) improves film quality and adhesion.

**Free standing ZnO NWs/Ag heterostructure and Its Photocatalytic Activity**

ZnO NWs grown on Ag

Photocatalytic activity: Degradation of organic dyes under UV light.

**Si Nanostructure by Metal-assisted Chemical Etching**

Metal acts as catalyst

Colorful Si nanostructures: Tunable optical properties.

**Surface Enhanced Raman Spectroscopy (SERS): 3D Si NWs/Ag**

High SERS enhancement factor

Stable and reproducible SERS signal

**Tip Enhanced Raman Spectroscopy (TERS)**

The key for TERS: High resolution, High stability, Tip-sizes less than 100 nm

TERS spectra of Si NWs/Ag

**Local Electronic Transport Behaviors of Graphene-Derived Nanostructures on Semiconductor Surface**

What will be done: Fabrication of graphene-derived nanostructures, Characterization of electronic transport behaviors.

**Surface Enhanced Raman Spectroscopy (SERS): Ag thin films**

-SERS substrate-: Ag thin film on SiO2/Si substrate

Structure and surface modification: Surface modification with organic molecules.

-SERS signal of Methylene blue-

-SERS Mapping-

“RSC Adv., 2016, 6, 7661-7667”

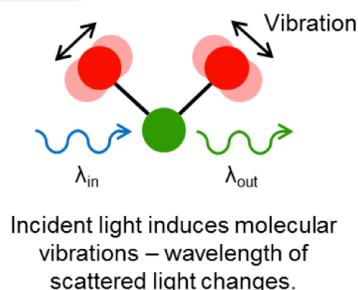
# Advantages of Raman Spectroscopy

*Chemical composition and structure of materials*

*Highly specific like a chemical fingerprint of a material*

*No sample preparation needed*

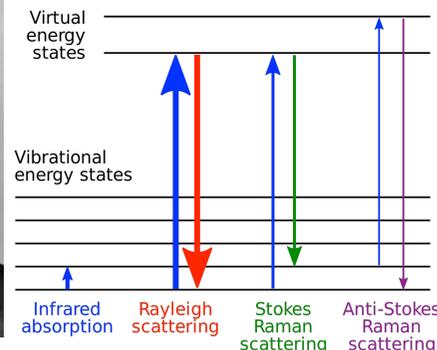
*Non-contacting and non-destructive*



Sir Chandrasekhara Venkata Raman



1928



*Raman spectra are acquired quickly within seconds*

*It works on almost all materials*

*Analyze through transparent containers and windows*

*Small volume analysis (< 1  $\mu\text{m}$  in diameter)*

*Samples can be analyzed through glass or a polymer packaging*

**Raman spectroscopy is a powerful technique for Nanocharacterization**

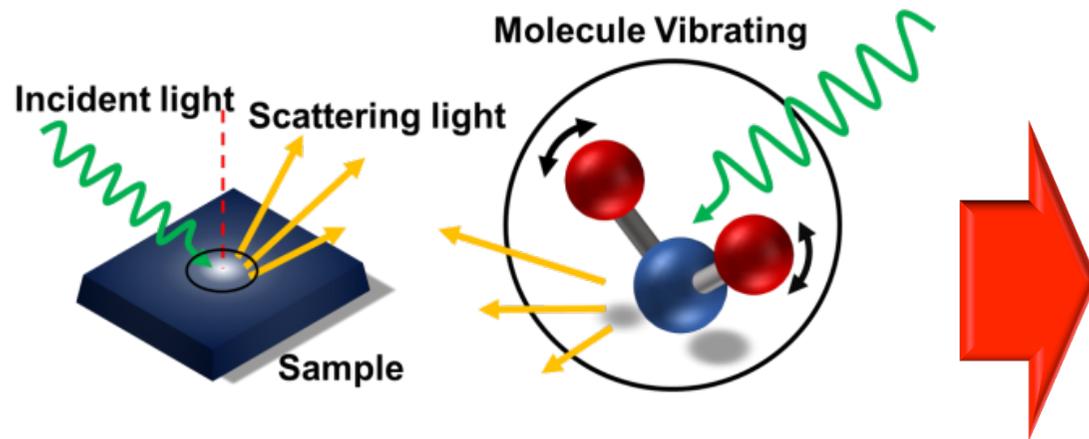
# Chemical composition analysis based on spectroscopy

	Raman Spectroscopy	Mid Infrared Spectroscopy	Near Infrared Spectroscopy
<b>Phenomenon</b>	Scattering	Absorption	Absorption
<b>Information</b>	Fundamental vibrations (down to low wavenumbers)	Fundamental vibrations	Overtone and combination bands
<b>Type of sample analyzed</b>	Organics and Inorganics	Organics and Inorganics	Organics
<b>Sample Preparation</b>	None	Normally required	Seldom
<b>Sample State</b>	Solids and liquids	Solids, liquids, and gases	Mainly solids
<b>Glass Vials</b>	Yes	No	Yes
<b>Water</b>	Yes	Water has a strong spectrum	Yes
<b>Remote Sampling</b>	Yes	No	Yes

Raman spectroscopy is a powerful technique for Nanocharacterization

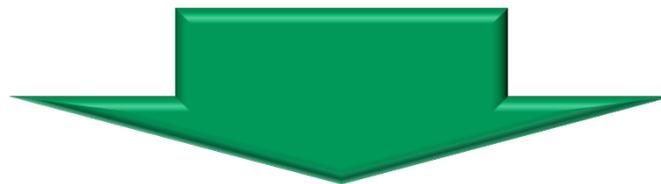
# Current problem of Raman Spectroscopy

## -Raman Signal-



***Problem: Difficult to detect low concentration samples***

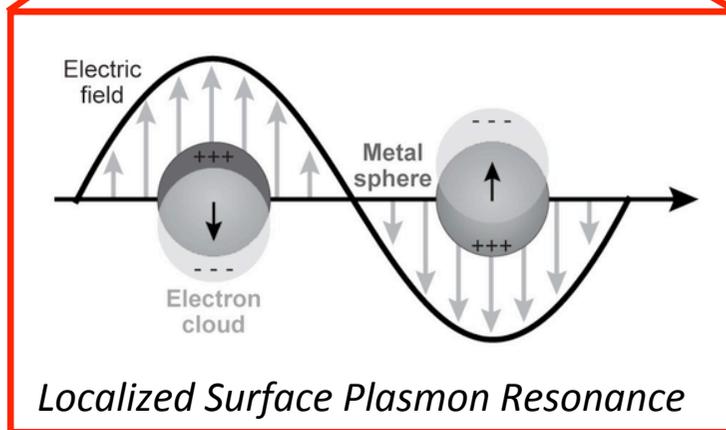
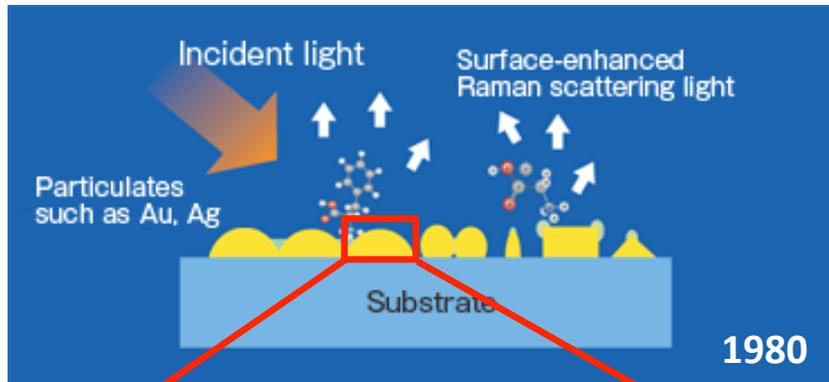
**Raman intensity lines are 0.001% (at most) of the source intensity**



**Solution: Raman signal amplifier is required**

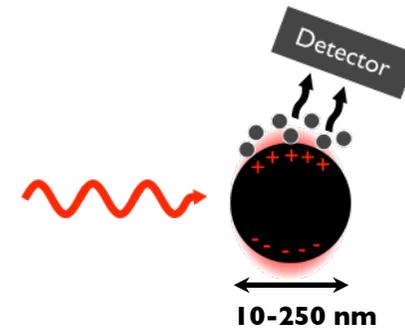
# Surface Enhanced Raman Spectroscopy (SERS)

## -SERS Signal-



Discovery of enhanced Raman signals ( $10^5$ - $10^6$ ) from molecules adsorbed on roughed Ag surfaces.

## -SERS Enhancement-



### **Chemical Enhancement**

Based on metal-molecule charge-transfer effects

### **Electromagnetic enhancement**

Coupled to *surface plasmon* excitation of metal nanostructures

### **Plasmon resonance leads to local field enhancement near the surface**

Adsorbed molecules see increased field

### **Raman signal enhancement (up to $10^{15}$ )**

Depends on local geometry of adsorption site

**SERS substrate is very promising for Raman signal enhancement**

# SERS substrate for chemical residual detection

## -Objective and Strategy-

- *Highly sensitive SERS substrate*
- *Uniformity detection*
- *Reusable/Low cost*

Today's talk

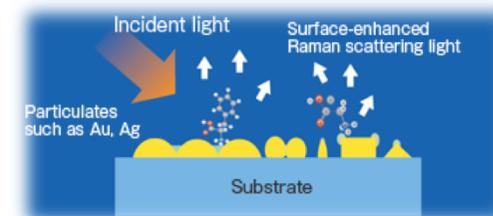
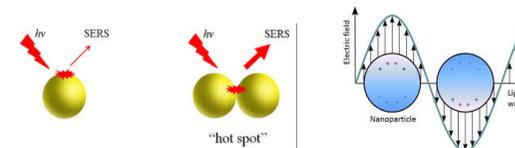
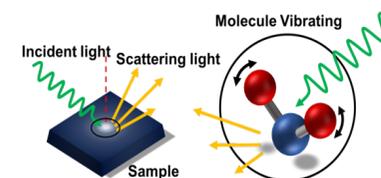
### 3. 3-D/hetero structure

### 2. Patterning

- *Highly sensitive SERS substrate*
- *Uniformity detection*

### 1. Thin films

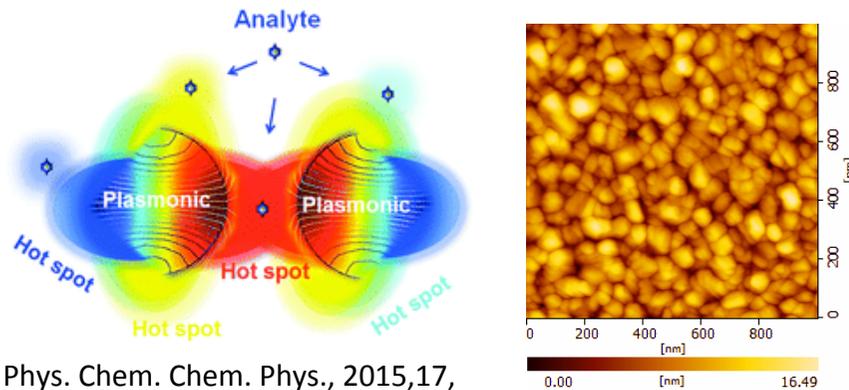
- *Highly sensitive SERS substrate*



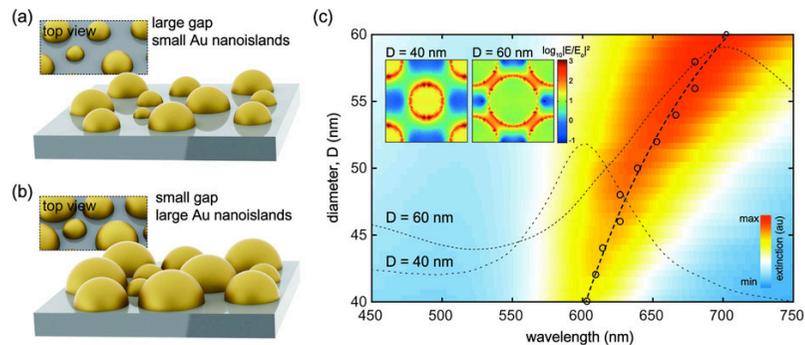
# SERS substrate based on Thin Films

-Crucial parameter for high sensitive SERS thin film-

**-Hot spot effect-**



Phys. Chem. Chem. Phys., 2015,17, 21072-21093



Scientific Reports 5, 14790 (2015)

- Texture orientation
- Roughness
- Grain size
- Gap between grain edges
- Density of grain
- Thickness

**Controllability on surface morphology and structure of Ag thin films is very important for high sensitive SERS substrate**

# Experimental

## -RF Magnetron Sputtering-



## “Metal Oxynitride Fabrication method”



(12) **United States Patent**  
Nukeaw et al.

(10) **Patent No.:** US 8,372,250 B2  
(45) **Date of Patent:** Feb. 12, 2013

(54) **GAS-TIMING METHOD FOR DEPOSITING  
OXYNITRIDE FILMS BY REACTIVE R.F.  
MAGNETRON SPUTTERING**

(56) **References Cited**

U.S. PATENT DOCUMENTS

(75) **Inventors:** Jiti Nukeaw, Bangkok (TH); Supanit Portheeraphat, Pathumthani (TH); Apichart Sunghong, Bangkok (TH)

4,289,797 A \* 9/1981 Akselrad ..... 427/539  
4,436,770 A \* 3/1984 Nishizawa et al. .... 427/570  
6,217,719 B1 \* 4/2001 Kanazawa et al. .... 204/192.12

\* cited by examiner

(73) **Assignees:** National Science and Technology Development Agency, Bangkok (TH); King Mongkut's Institute of Technology Ladkrabang, Bangkok (TH)

Primary Examiner — Keith Hendricks  
Assistant Examiner — Jason M Berman

(74) **Attorney, Agent, or Firm** — Sites & Harbison, PLLC; Juan Carlos A. Marquez, Esq.; Stephen J. Wever, Esq.

**NSTDA U.S. Patent**

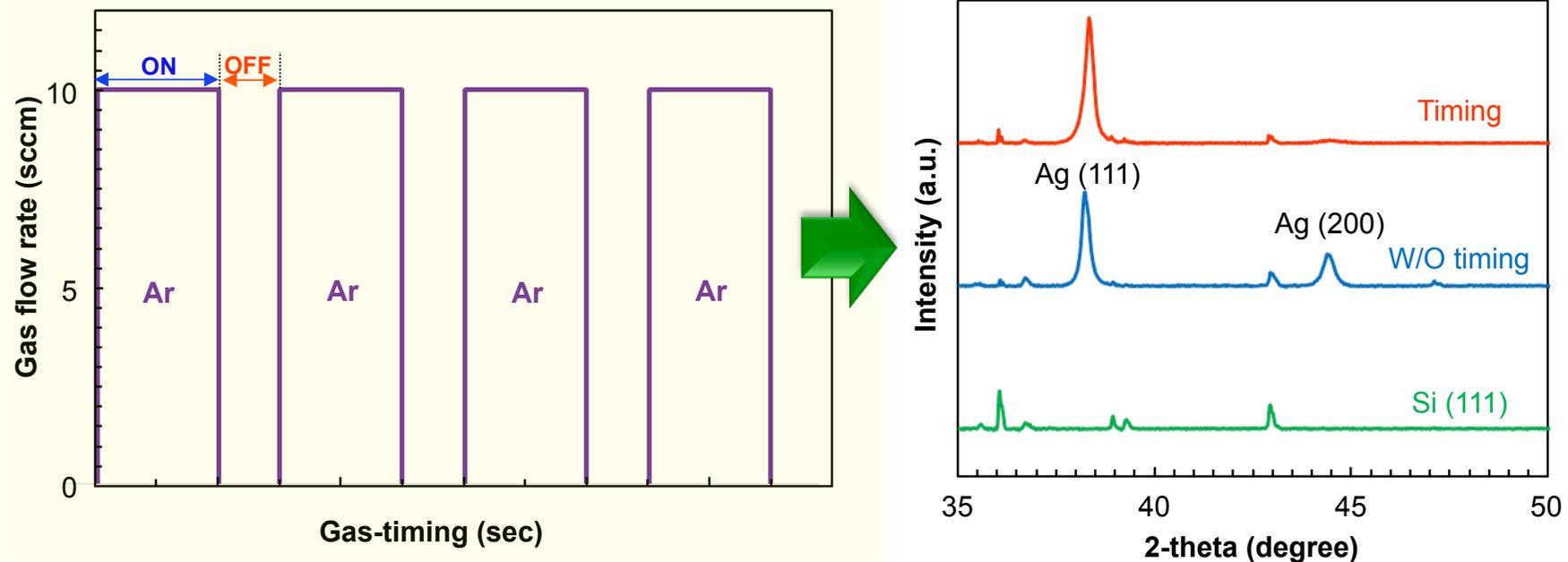
## -Advantages-

- Large area coating with high uniformity
- Low Temperature Operation
- High adhesion film and substrate
- Reproducible and cleaning process
- Friendly Environmental System

**Can we control structure and morphology of Ag thin films via GT technique?**

# Can we control structure and morphology of Ag thin films via GT technique?

## -Texture orientation-

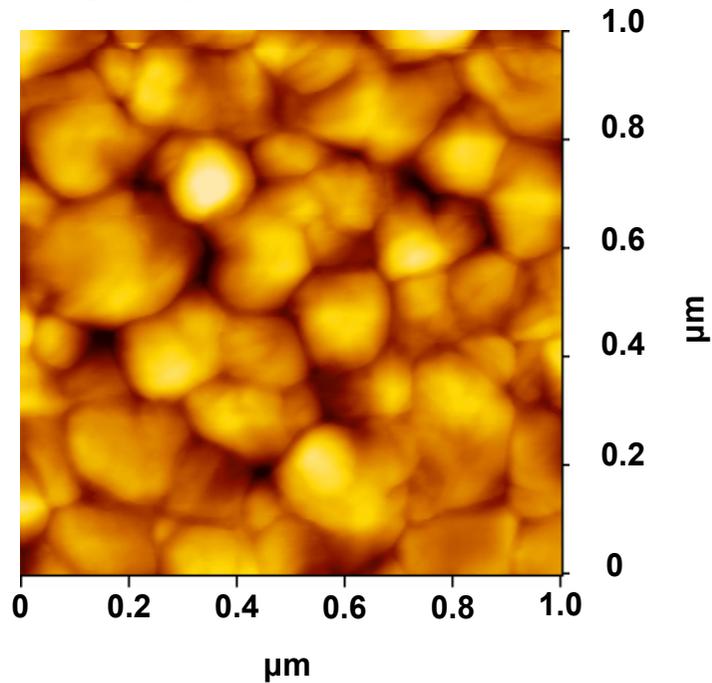


High order texture of Ag (111) thin films could be fabricated by using gas-timing rf magnetron sputtering technique

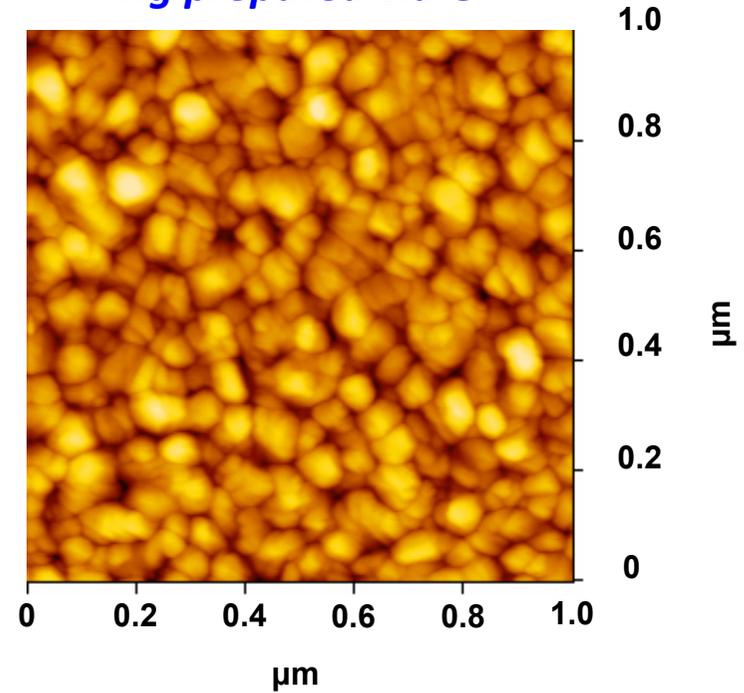
# Can we control structure and morphology of Ag thin films via GT technique?

## -Morphology-

*-Ag prepared via w/o GT-*

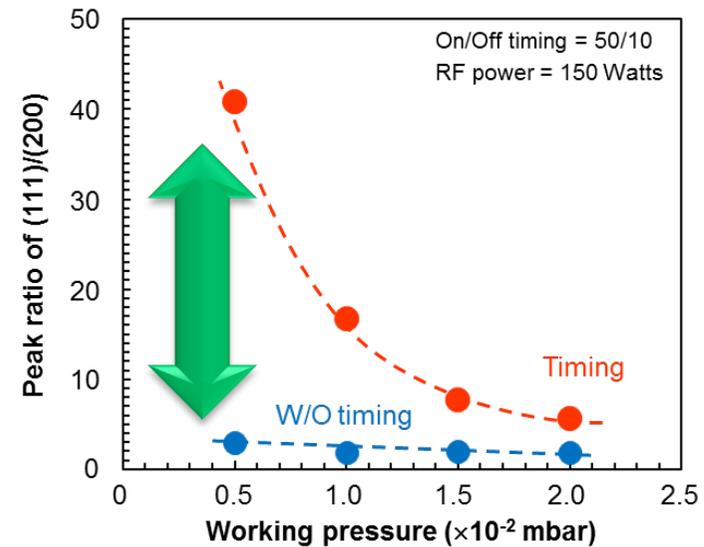
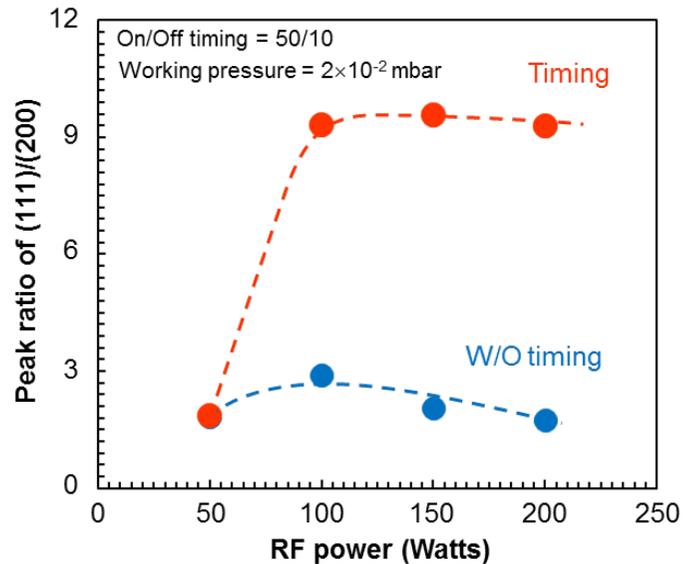
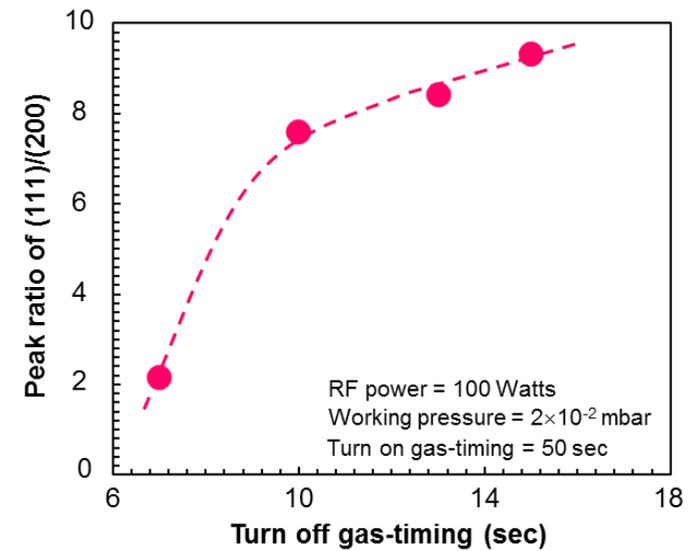
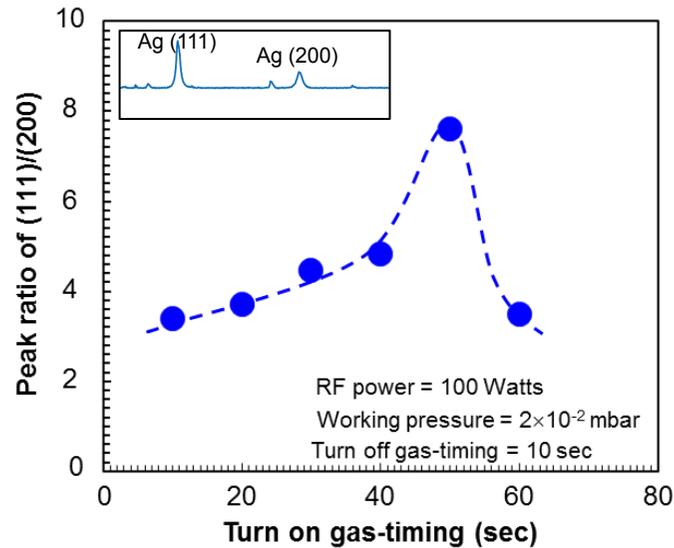


*-Ag prepared via GT-*



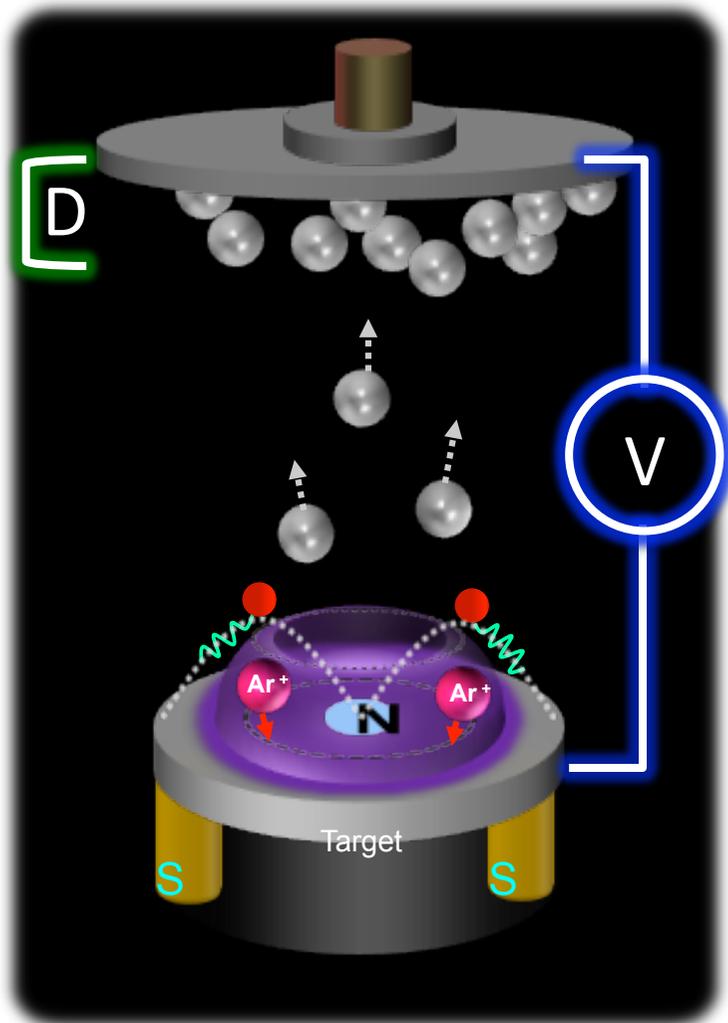
**Smaller grain size could be obtain when GT technique is utilized**

# Peak intensity of (111)/(200) ratio of Ag thin films

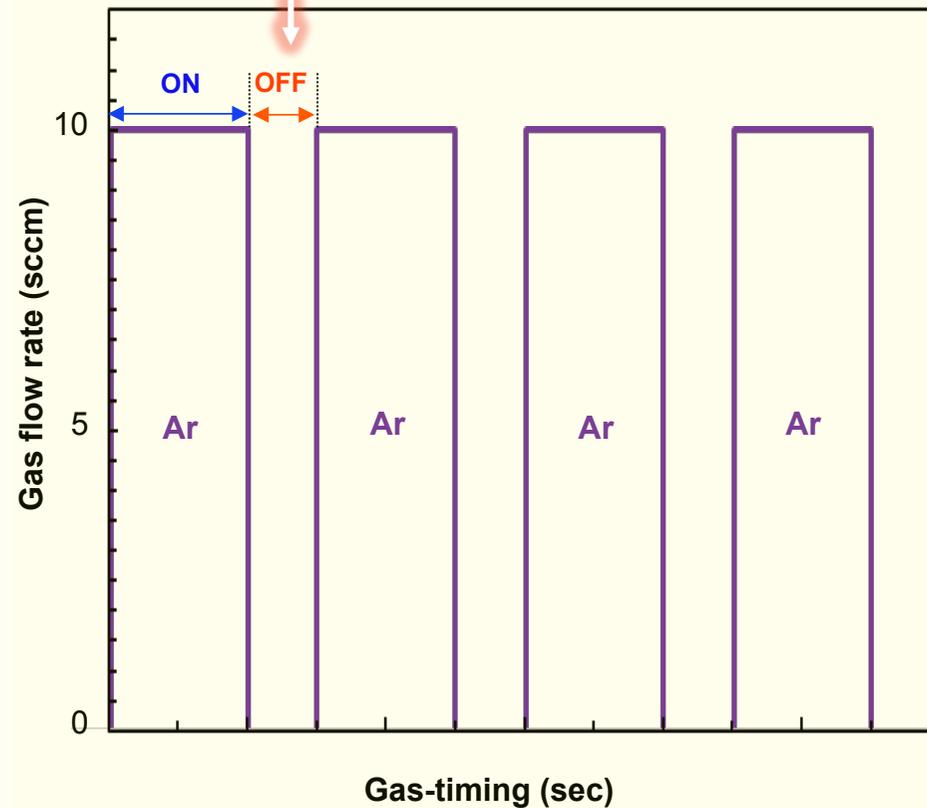


**How does gas-timing technique enhance the crystal growth?**

# How does gas-timing technique enhance the crystal growth?



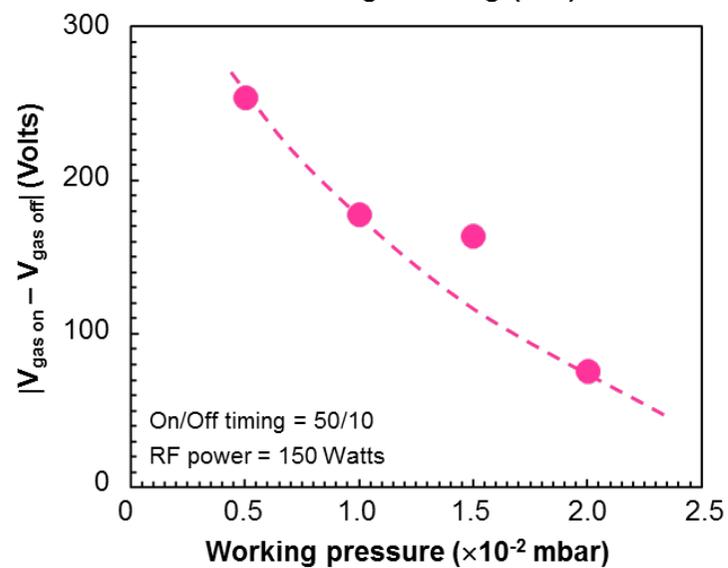
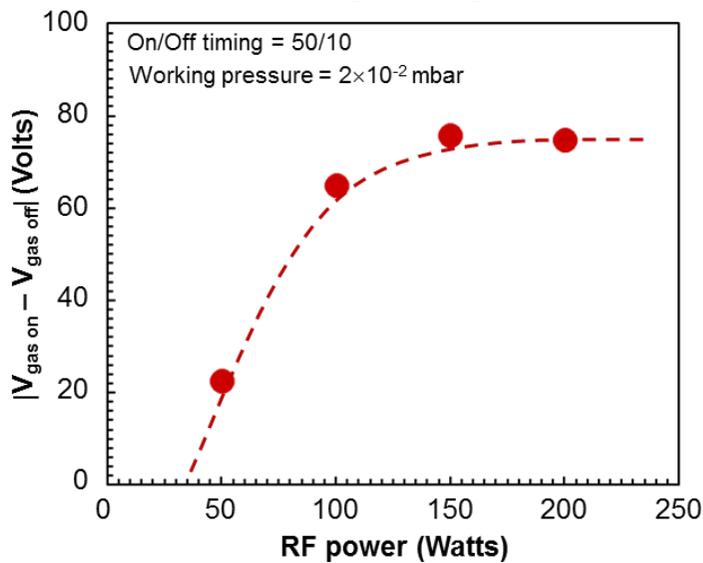
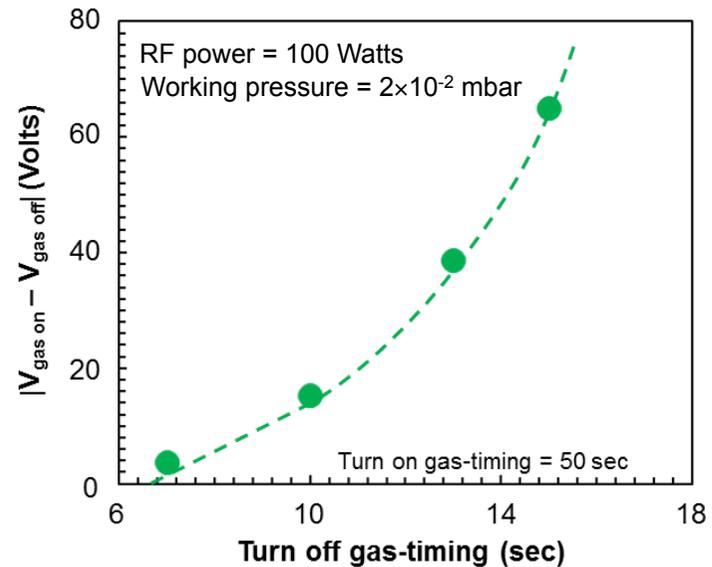
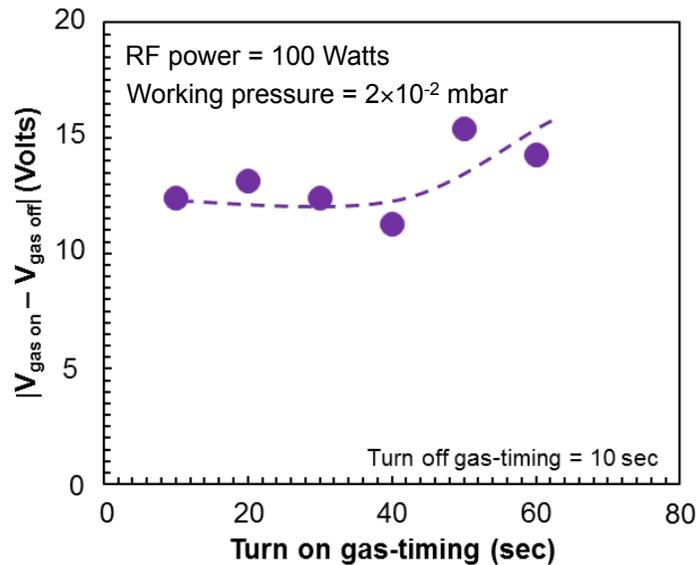
Lower sputtered atom with constant sputter energy



$$\text{Energy per atom} = \frac{\text{Total sputtered energy}}{\text{Total sputter gas atom}}$$

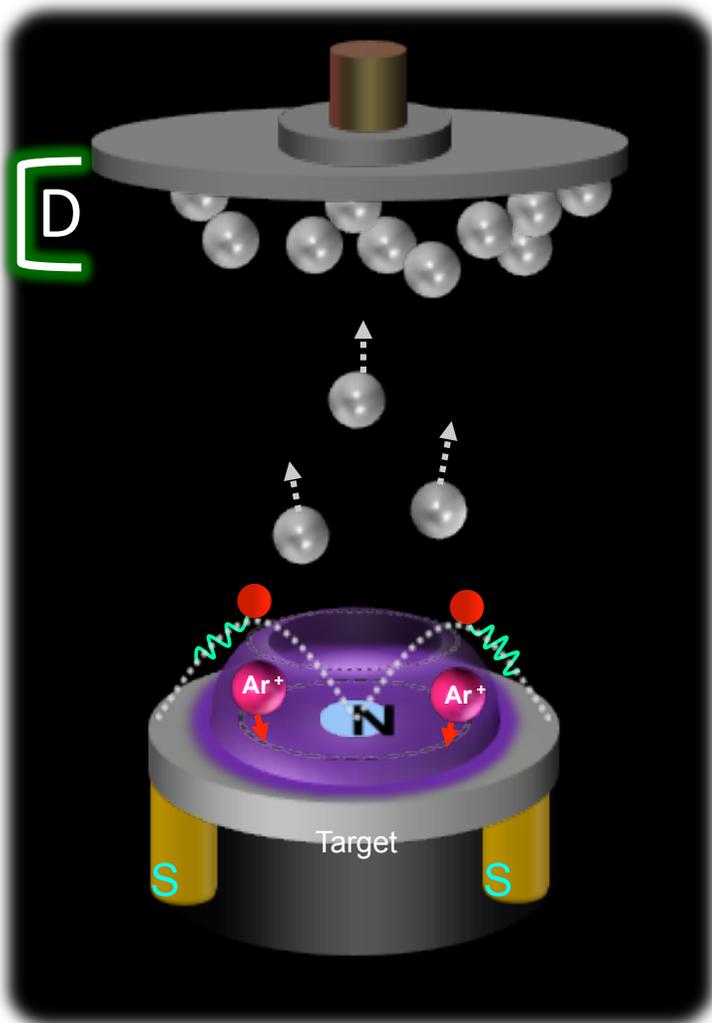
Higher energy of sputtered atoms might be raised during turn-off sequence.

# Difference in RF bias voltage between turn-on timing and turn-off timing

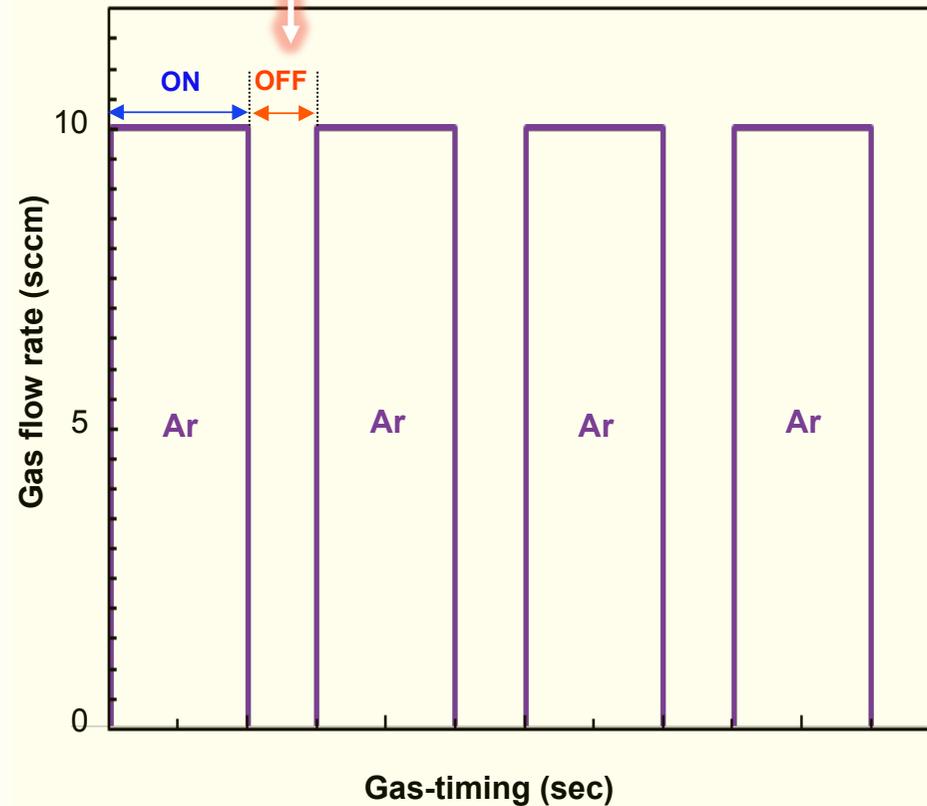


**Gas-timing technique strongly enhanced the total sputtered energy**

# How does gas-timing technique enhance the crystal growth?



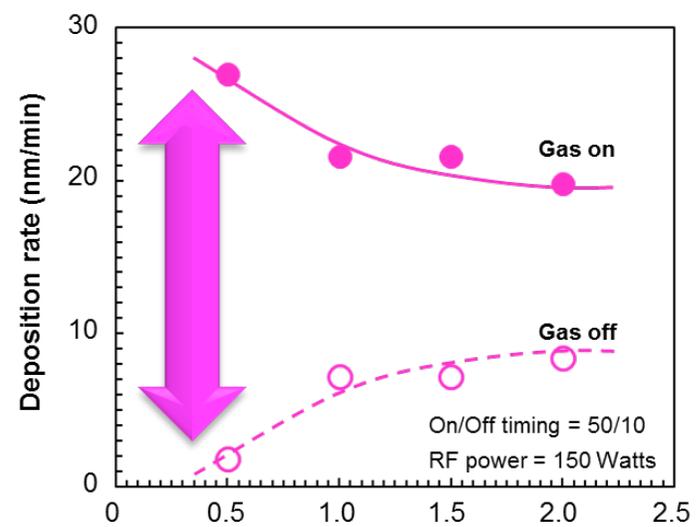
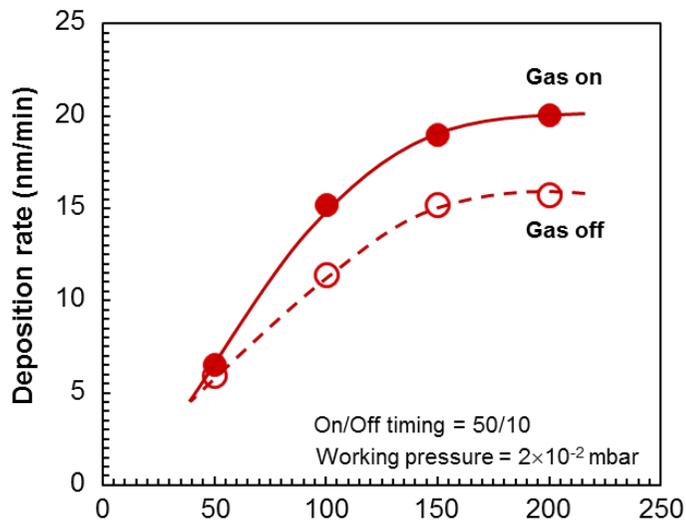
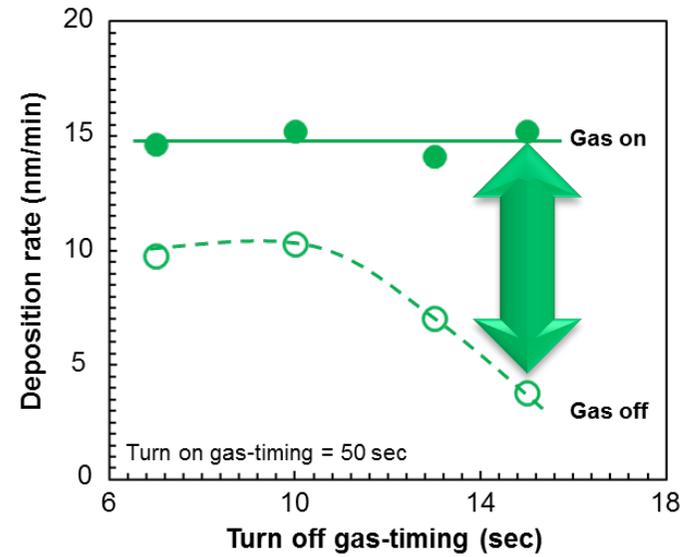
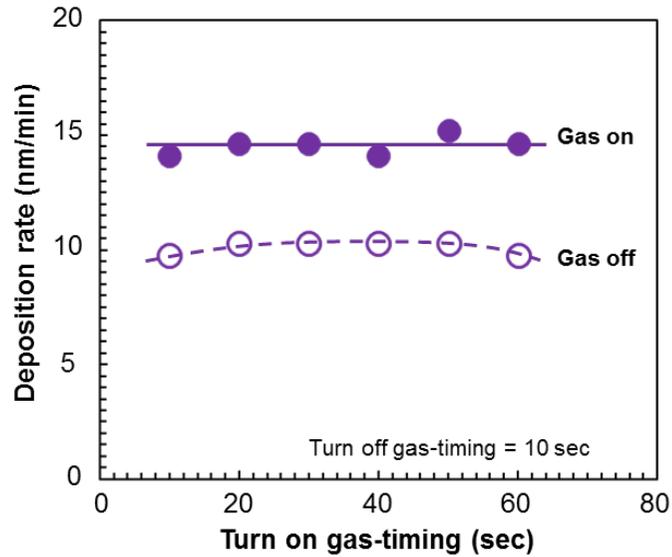
Lower sputtered atom with constant sputter energy



$$\text{Energy per atom} = \frac{\text{Total sputtered energy}}{\text{Total sputter gas atom}}$$

Higher energy of sputtered atoms might be raised during turn-off sequence.

# Deposition rate of Ag thin films between turn-on timing and turn-off timing



**What is the origin?**

# What is the origin?

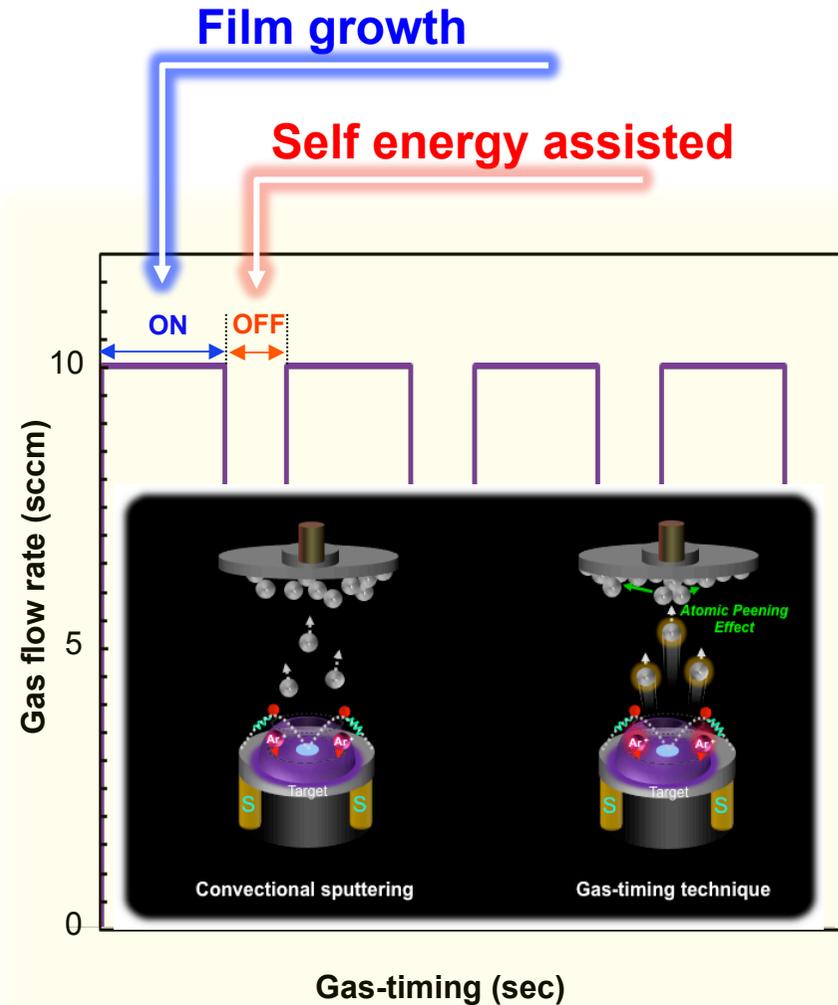
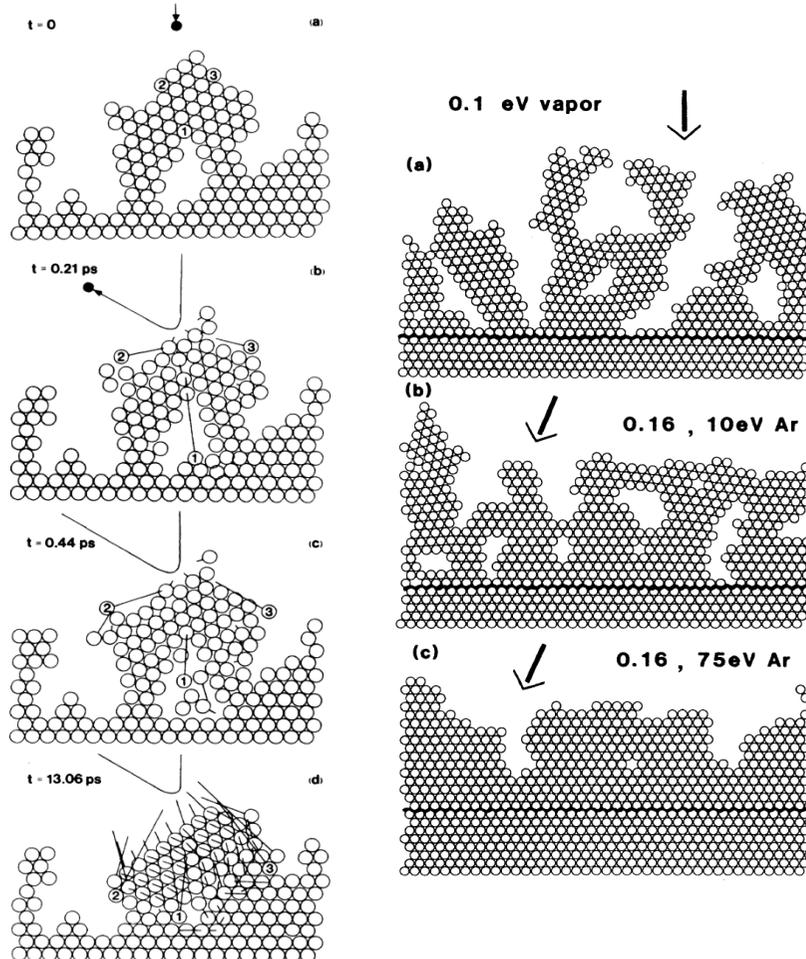
## -Atomic peening mechanism-

Ion-beam-induced epitaxial vapor-phase growth: A molecular-dynamics study

Karl-Heinz Müller

Commonwealth Scientific and Industrial Research Organization, Division of Applied Physics,  
National Measurement Laboratory, Sydney, Australia 2070

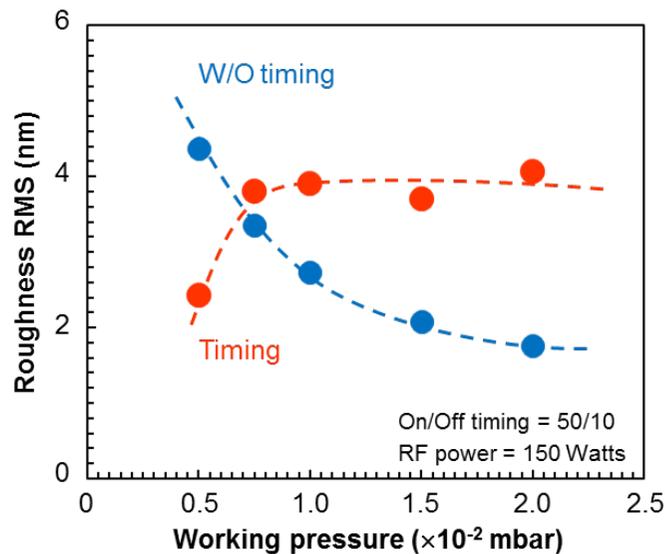
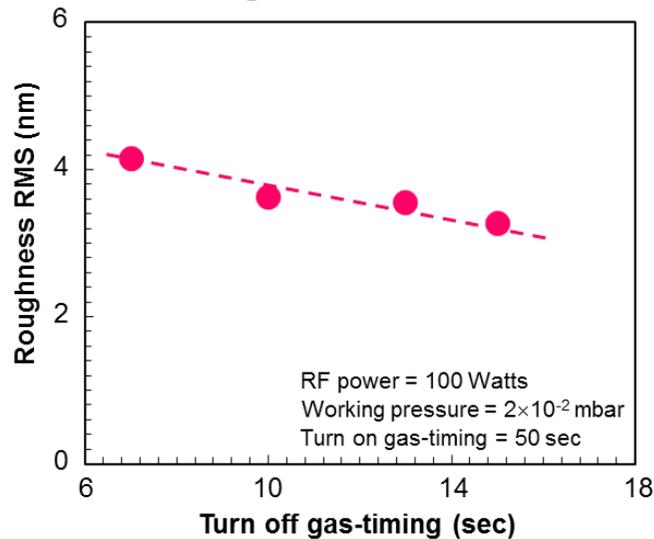
(Received 5 May 1986; revised manuscript received 24 December 1986)



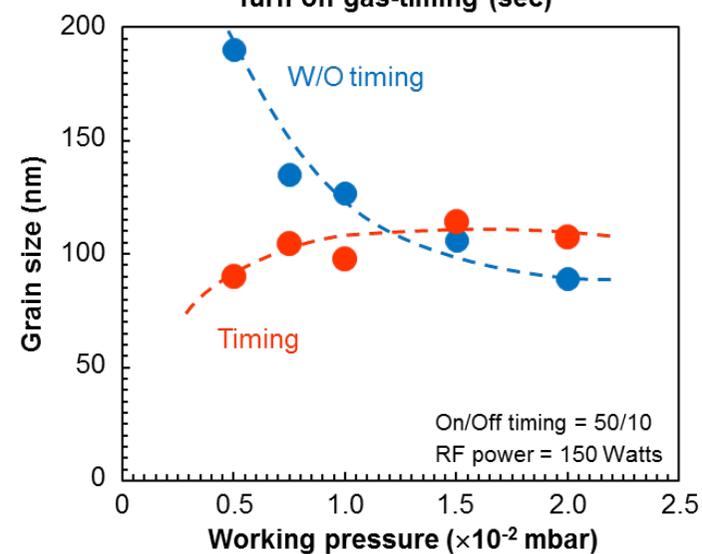
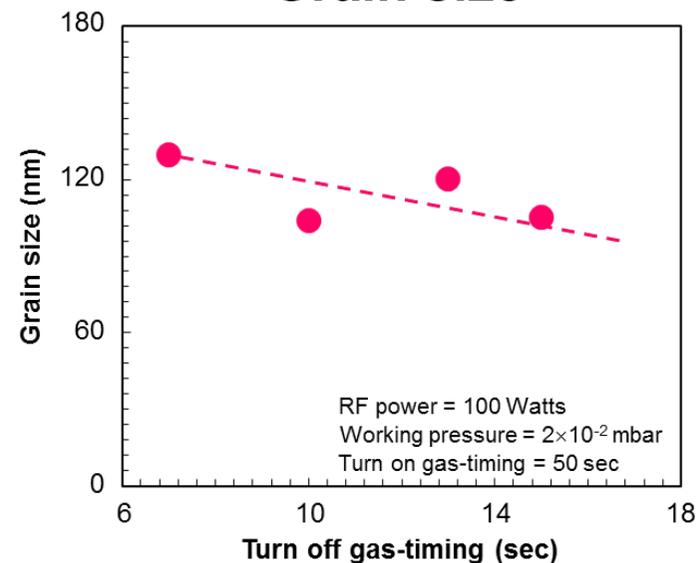
Self energy assisted might be provided by gas-timing technique

# Morphology of Ag thin films

## -Roughness RMS-

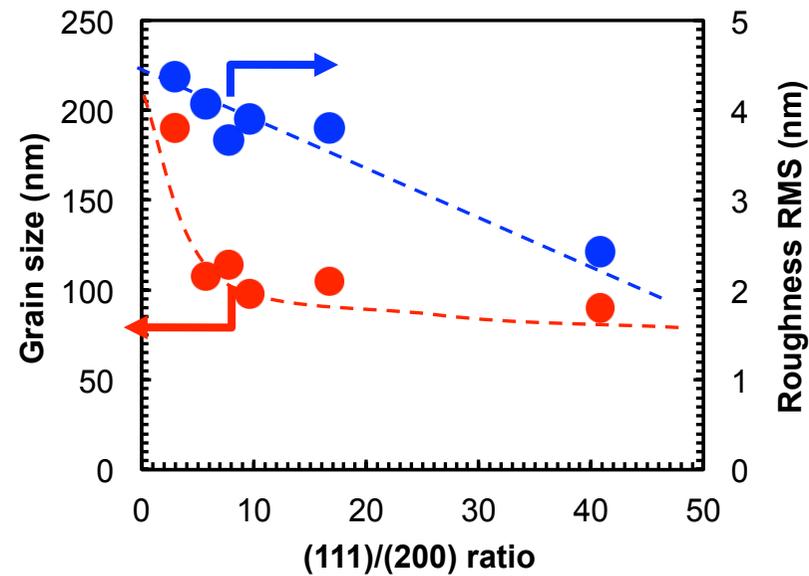
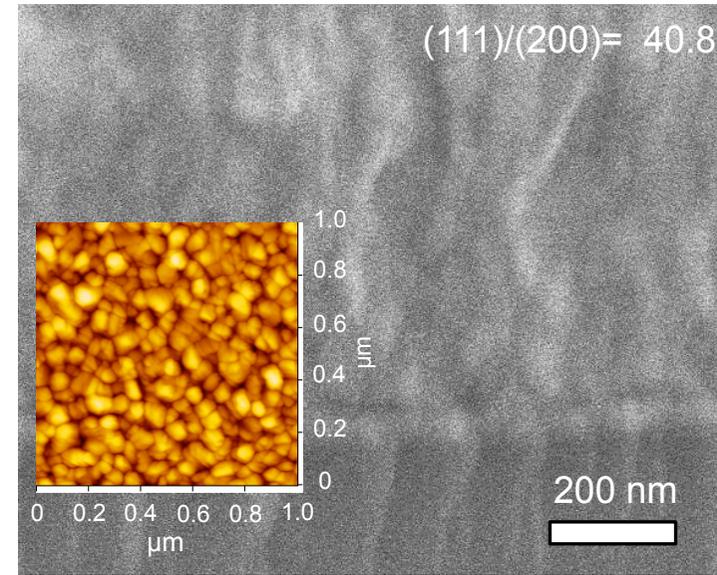
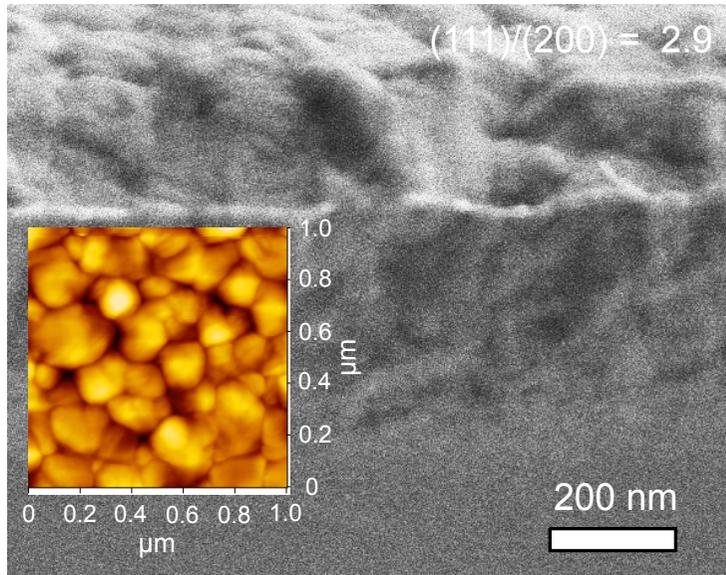


## -Grain size-



Dense structure of Ag (111) might be obtained via adatom diffusion via high energy during sputter deposition

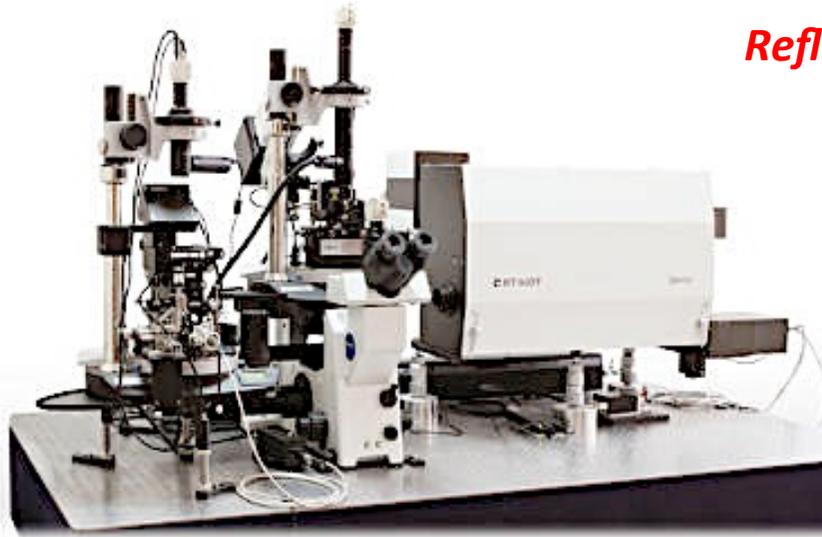
# Morphology vs. Texture orientation



**Controllability on texture orientation and morphology can be archived via GT technique**

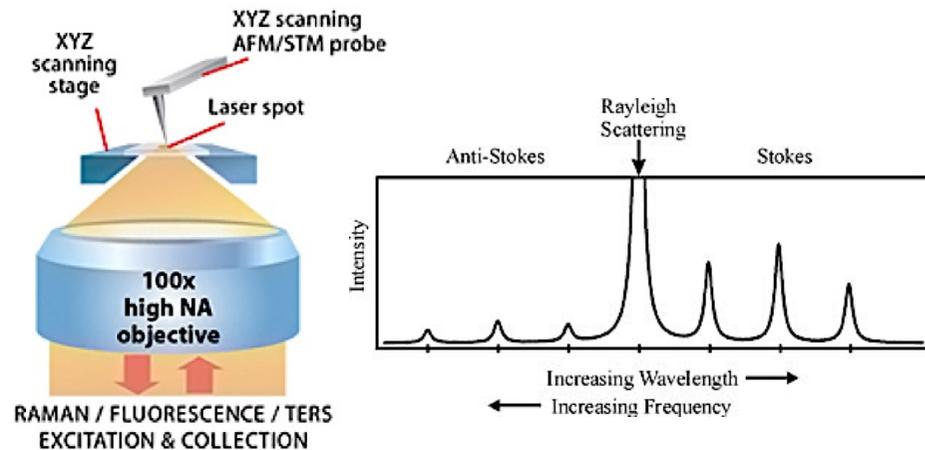
# SERS Measurement

-NT-MDT NTEGRA SPECTRA-



*Reflection Mode*

- Excitation wavelength of 532 nm
- Charge-coupled device (CCD) with a resolution of  $4 \text{ cm}^{-1}$

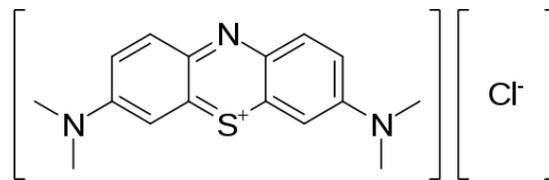


-Raman Active Molecule-

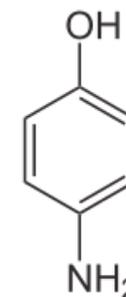
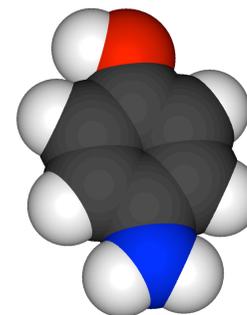
*Methylene Blue (MB)*



$10^{-3}$  to  $10^{-13}$  M



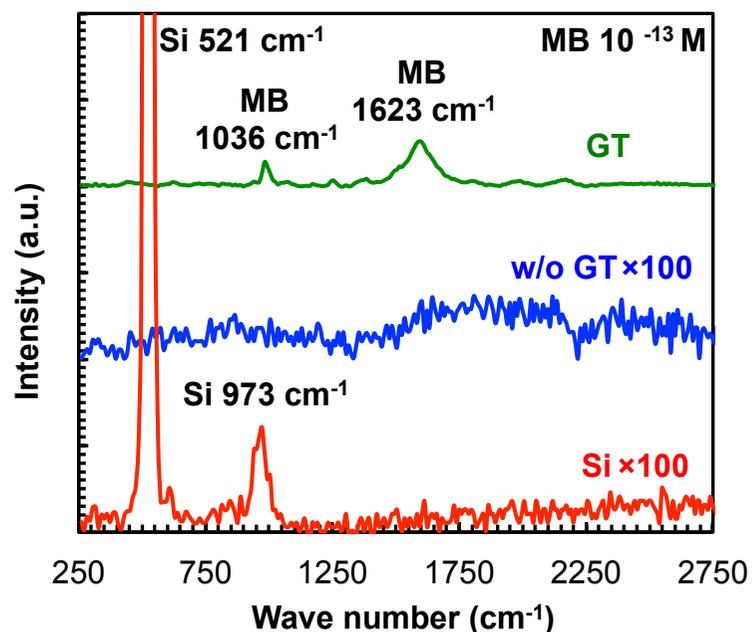
*4-Aminophenol*



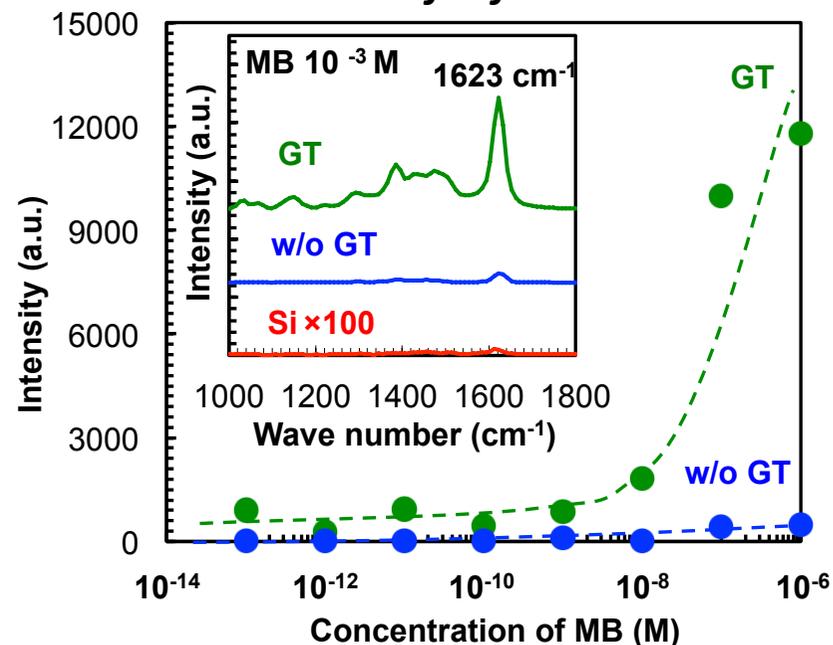
$10^{-3}$  to  $10^{-12}$  M

# SERS signal of GT vs. Conventional

-Raman spectra of methylene blue (MB) droplets at concentration of  $10^{-13}$  M-



- SERS intensity collected at Raman shift of  $1626 \text{ cm}^{-1}$ -



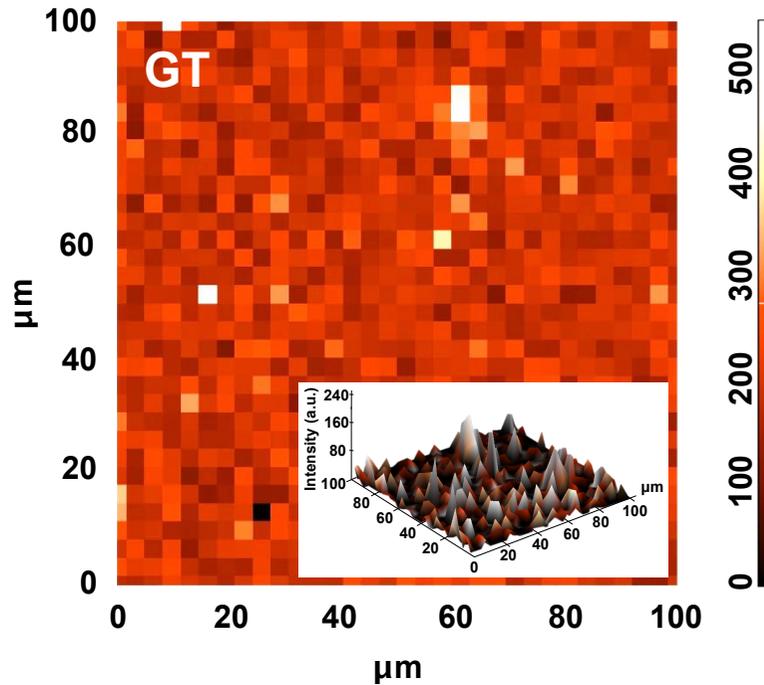
-Morphology of Ag thin films-

Ag thin films SERS substrate	RMS Roughness (nm)	Grain size (nm)	Gab between grain edge (nm)	Density of grain (grain/ $\mu\text{m}^2$ )
GT technique	2.4	80.3	55.2	306
Conventional sputtering	4.4	190.5	85.6	90

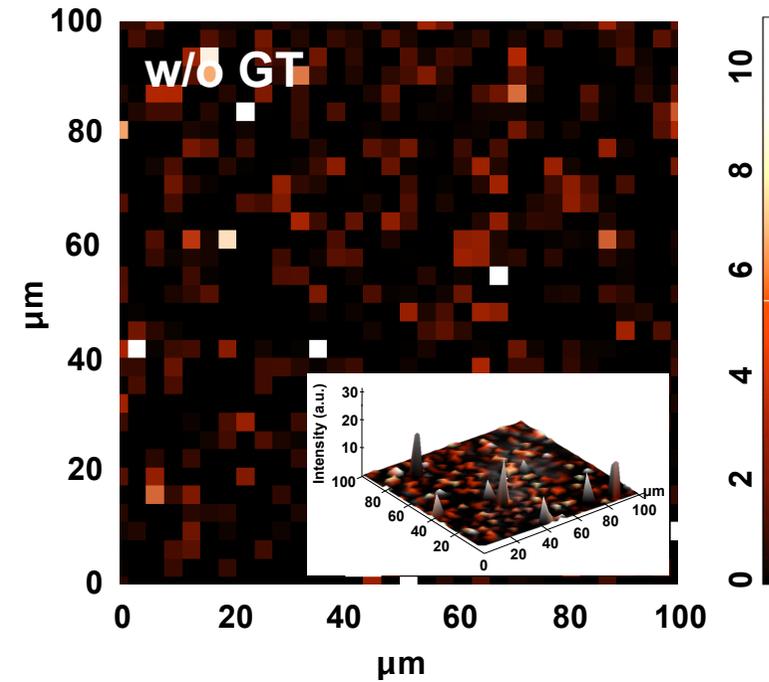
**High sensitivity SERS substrate is successfully fabricated via GT technique**

# SERS mapping: Distribution of SERS signal

*-SERS Mapping of GT substrate-*



*-SERS Mapping of Conventional substrate-*



$$EF = \frac{I_{SERS}}{I_{Ref}} \frac{N_{Ref}}{N_{SERS}}$$

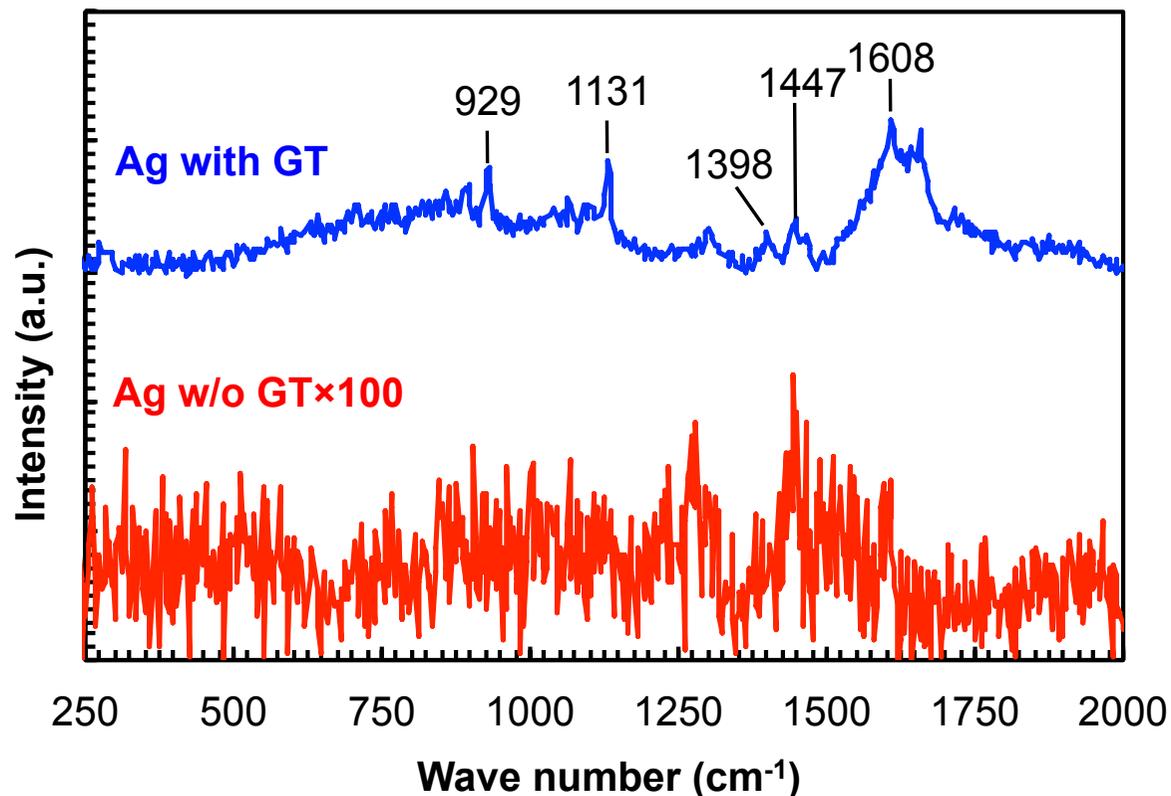


$$EF_{GT} = 3.4 \times 10^5 \text{ and } EF_{con} = 1.4 \times 10^4$$

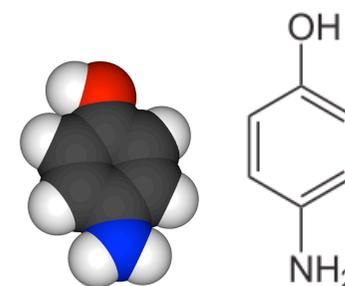
**Uniformity of SERS signals can be accomplished when the SERS substrate fabricated by the GT technique is utilized.**

# Are we confident with our SERS substrate?

*-Raman spectra of 4-ATP droplets at concentration of  $10^{-12}$  M-*



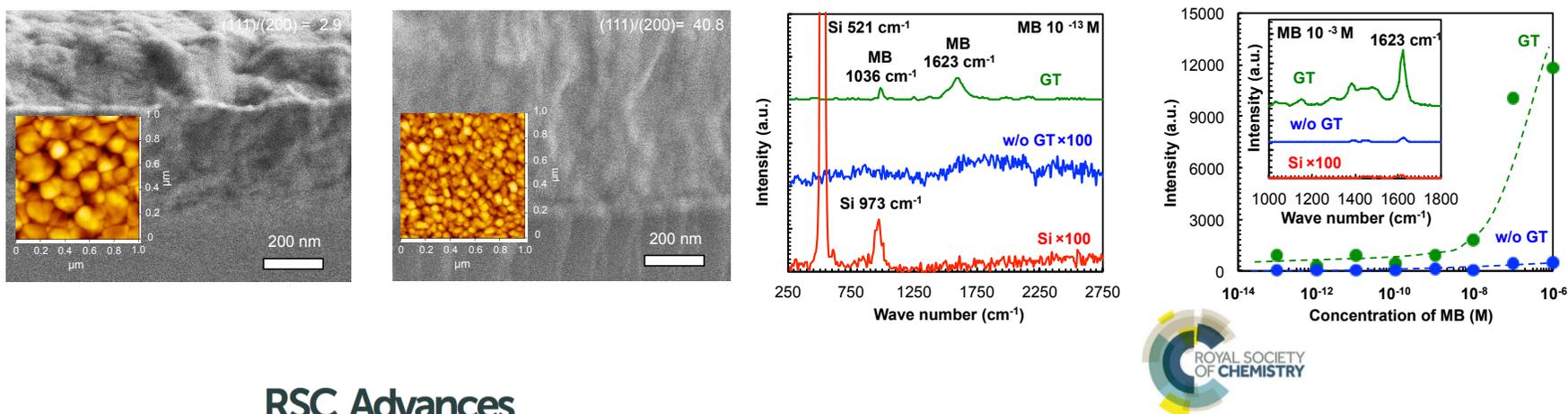
*-4-Aminophenol-*



**Ag thin films prepared by GT technique are promising for SERS activities**

# Summary

1. The controllability on structure and morphology of Ag thin film is achieved by using GT technique
2. High sensitive and uniform SERS thin film substrate is demonstrated



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## Texture orientation of silver thin films grown *via* gas-timing radio frequency magnetron sputtering and their SERS activity†

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**Thank you very much for your attention**

