Crucial role of Nanomaterial Development for Nanocharacterization

Annop Klamchuen

Nano Characterization Laboratory (NCL)
National Nanotechnology Center (NANOTEC), Thailand

ABOUT US....

THAILAND

PATHUMTHANI PROVINCE

CENTRAL OFFICE

INNOVATION CLUSTER BUILDING

SIRINDHORN SCIENCE HOME

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

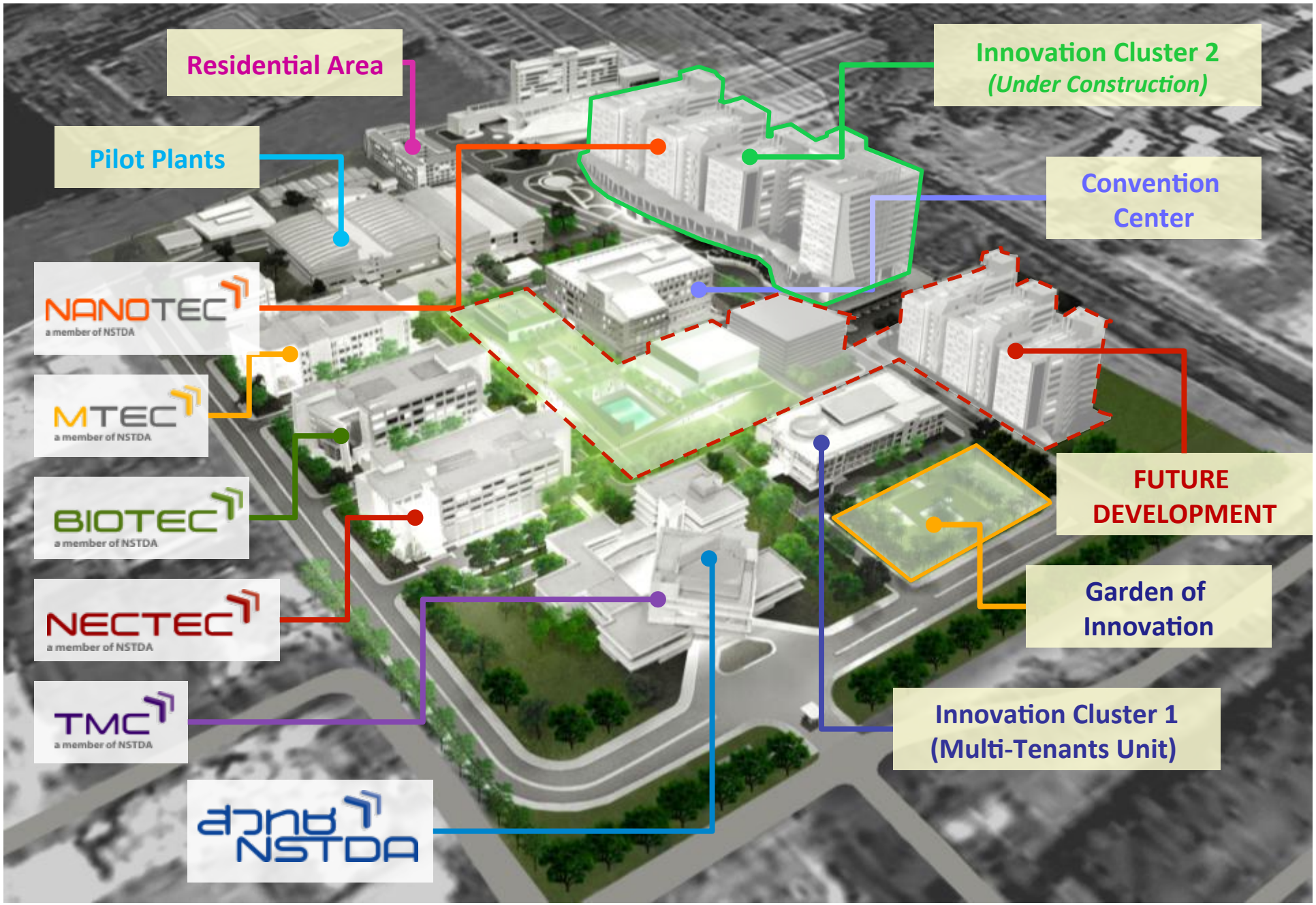
NANOTEC
a member of NSTDA

National Nanotechnology Center

TMC
a member of NSTDA

Technology Management Centre

S&T Community in TSP



NANOTEC
a member of NSTDA

10th anniversary
NANOTEC
a member of NSTDA

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

NSM

Dr.Wiyong Kangwansupamonkon
Research Unit Director

MAT

Dr.Kajornsak Faungnawakij
Research Unit Director

FUN

Dr.Udom Asawapirom
Research Unit Director

Nanotechnology for Life & Health Science Research Unit	Nanostructure & Nanometrology Research Unit	Nanomaterials & Nanosystems Engineering Research Unit	Functional Nanomaterials & Assembly Research Unit
Nano Delivery System (NDS)	Nano Characterization (NCL)	Nanomaterial for Energy & Catalysis (NEC)	Functional Nanomaterial & Interfaces (FNI)
Nano Molecular Target Discovery (TDI)	Nano Safety & Risk Assessment (SRA)	Integrated Nano System (INS)	Engineering & Manufacturing (ENM)
Nano Cosmeceutical (NCM)	Nano Agro & Food Innovation (NAF)	Nano Scale Simulation (SIM)	Nanostructure & Functional Assembly (NFA)
	Hybrid Nanostructure & Nanocomposites (HNN)	Nanoengineered Soft Materials for Green Environment (SOF)	Nano Functional Textile (NFT)

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Nano Products in Market Place

Many nano products are being developed and marketed without detailed characterization nor prior review and approval of their efficacy and safety.

LACK OF INFORMATION

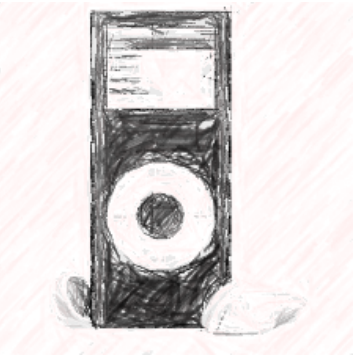
REAL or FAKE ?

REAL with QUALITY ?

REAL with SAFETY ?

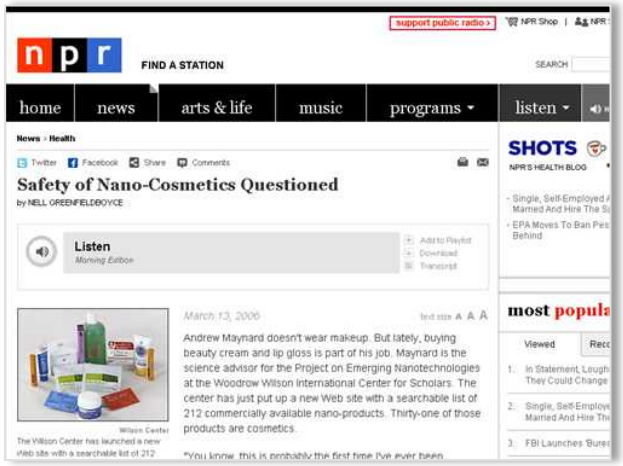
INFORMATION OF THE TEST ITEM (CLOSED TO) CORRECT ONES

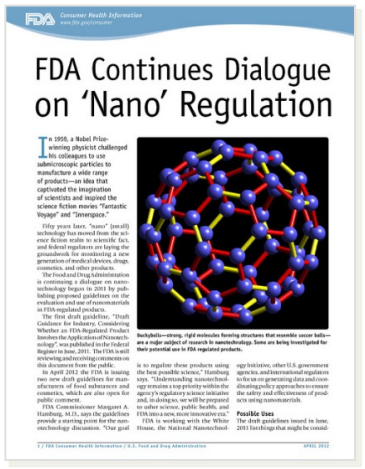
- WHICH PART IS CLAIMED NANO ?
- COMPOSITION OF THE NANO
- FUNCTION CLAIMED



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





Nanotechnology Value Chain

Nanomaterials → **Nanointermediates** → **Nano-enable products**

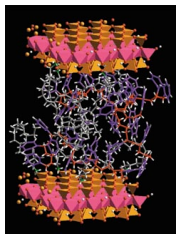
Nanoscale structures in unprocessed form

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

NanoMARKS

Targeted Nanoproducts
- Cosmetics
- Food
- Petrochemicals

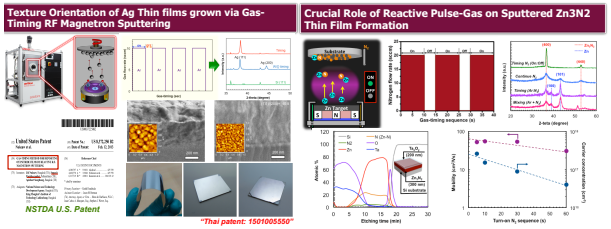
Sample tested for : NANOTECHNOLOGY
Anti-bacteria
Water repellance
Brand : .... Model : .....
Nano
สมาคมนาโนเทคโนโลยีแห่งประเทศไทย
Nanotechnology Association of Thailand

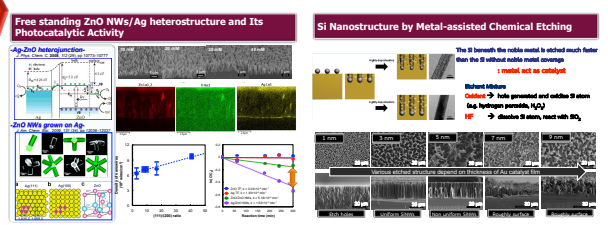
Product labeling

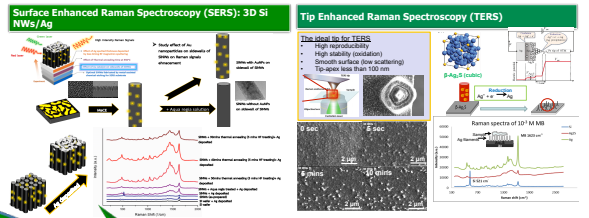
Our Research & Development Focus

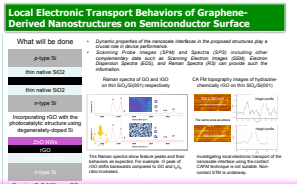
"Measurement method/test development for Nanocharaterization"

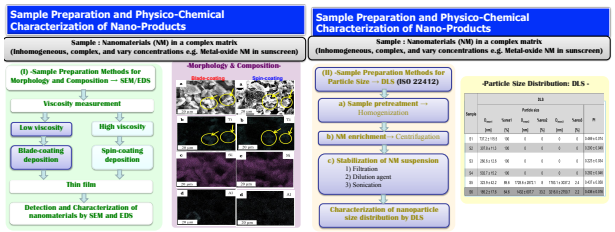
Material fabrication & Design





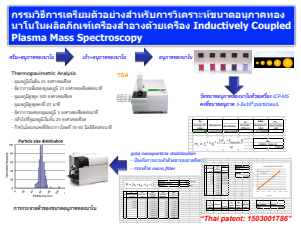


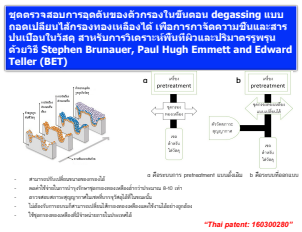




R & D

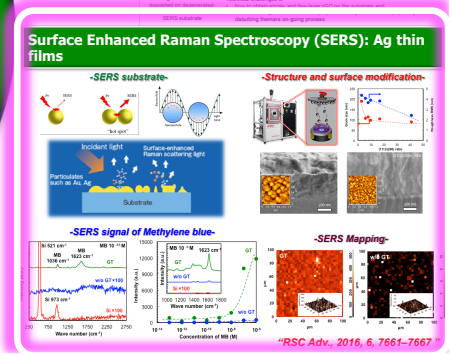
Sample Preparation method for Characterization





Characterization technique improvement

"Raman spectroscopy"



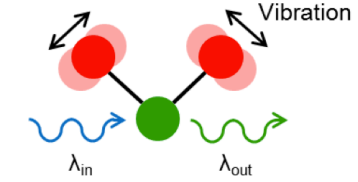
Advantages of Raman Spectroscopy

Chemical composition and structure of materials

Highly specific like a chemical fingerprint of a material

No sample preparation needed

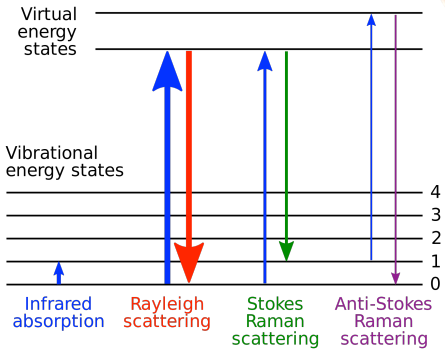
Non-contacting and non-destructive



Incident light induces molecular vibrations – wavelength of scattered light changes.

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 µm in diameter)

Samples can be analyzed through glass or a polymer packaging

Raman spectroscopy is a powerful technique for Nanocharacterization

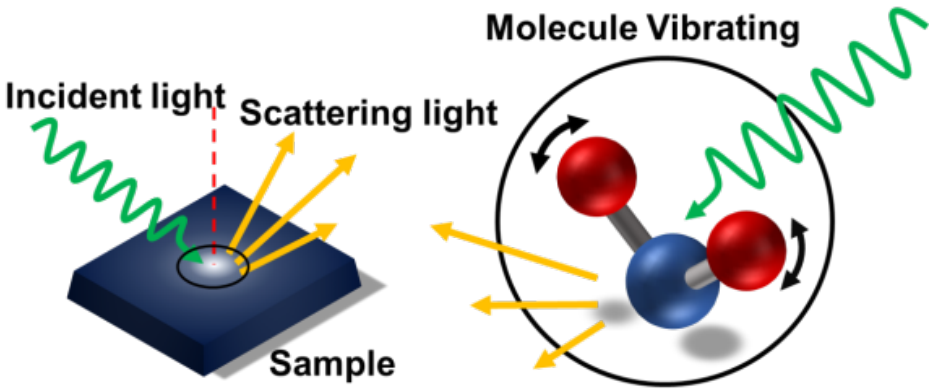
Chemical composition analysis based on spectroscopy

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

Raman spectroscopy is a powerful technique for Nanocharacterization

Current problem of Raman Spectroscopy

-Raman Signal-



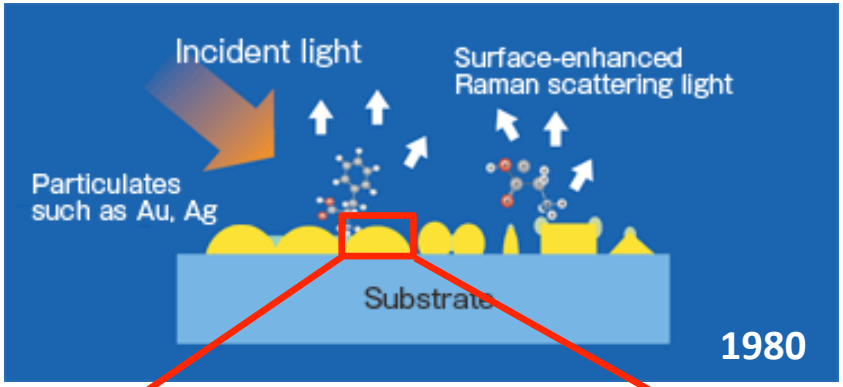
Problem: ***Difficult to detect low concentration samples***

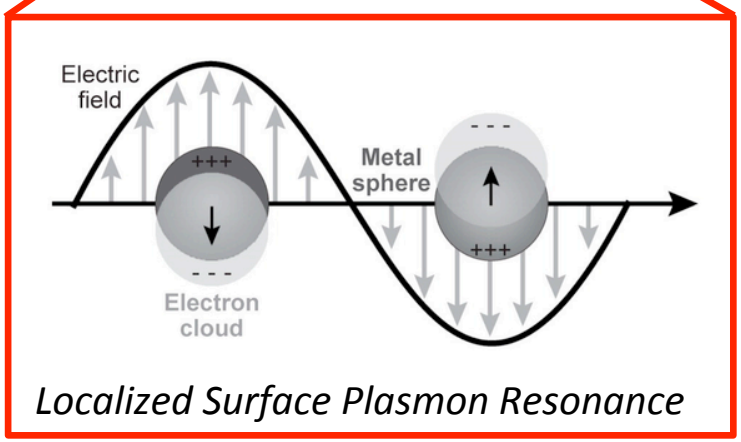
Raman intensity lines are 0.001% (at most) of the source intensity

Solution: Raman signal amplifier is required

Surface Enhanced Raman Spectroscopy (SERS)

-SERS Signal-

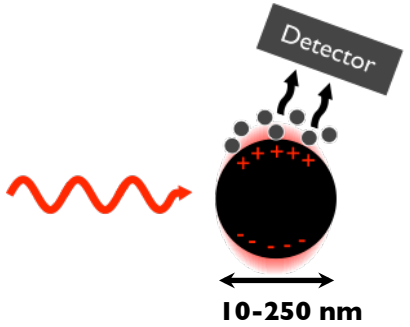




Localized Surface Plasmon Resonance

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})

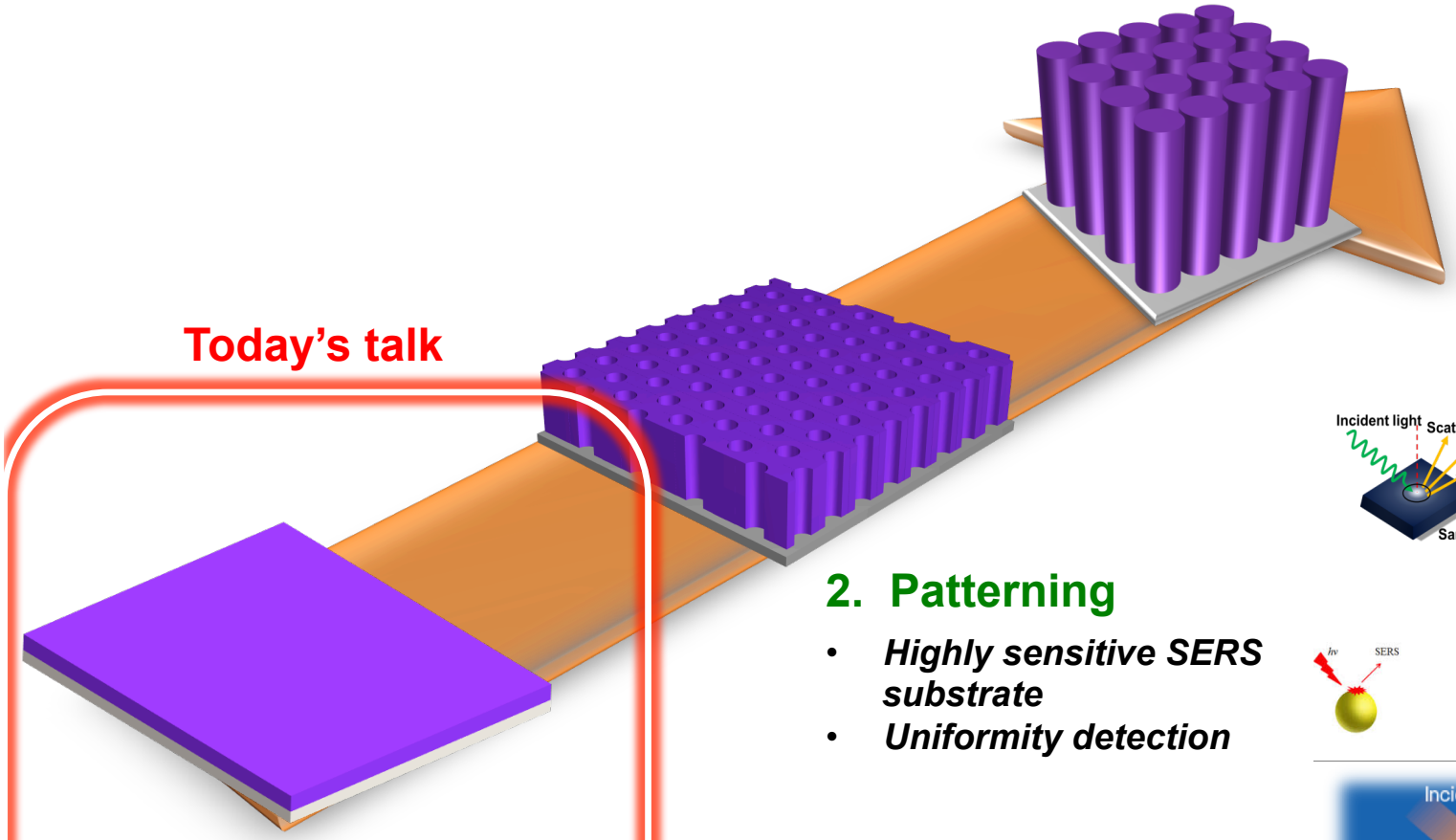
Depends on local geometry of adsorption site

SERS substrate is very promising for Raman signal enhancement

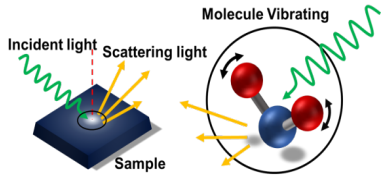
SERS substrate for chemical residual detection

-Objective and Strategy-

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



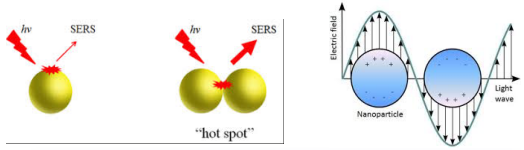
3. 3-D/hetero structure

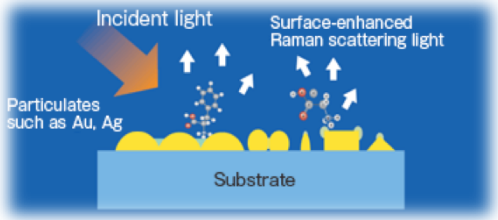


Today's talk

2. Patterning

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





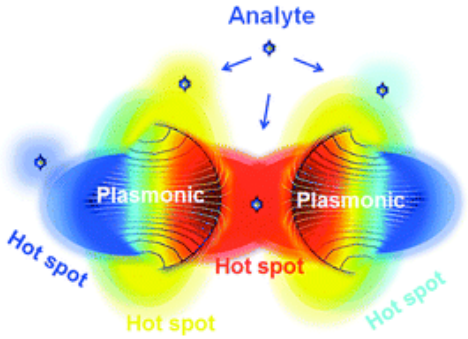
1. Thin films

- *Highly sensitive SERS substrate*

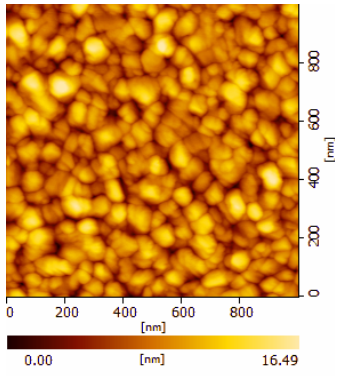
SERS substrate based on Thin Films

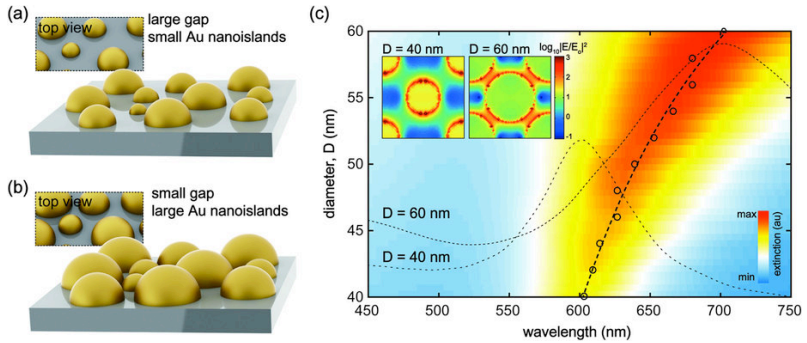
-Crucial parameter for high sensitive SERS thin film-

-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**

(75) Inventors: **Jiti Nukeaw**, Bangkok (TH); **Supanit Porntheeraphat**, Pathumthani (TH); **Apichart Sungthong**, Bangkok (TH)

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

(56) **References Cited**

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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

Primary Examiner — Keith Hendricks
Assistant Examiner — Jason M Berman
(74) *Attorney, Agent, or Firm* — Stites & Harbison, PLLC; Juan Carlos A. Marquez, Esq.; Stephen J. Wever, Esq.

NSTDA U.S. Patent

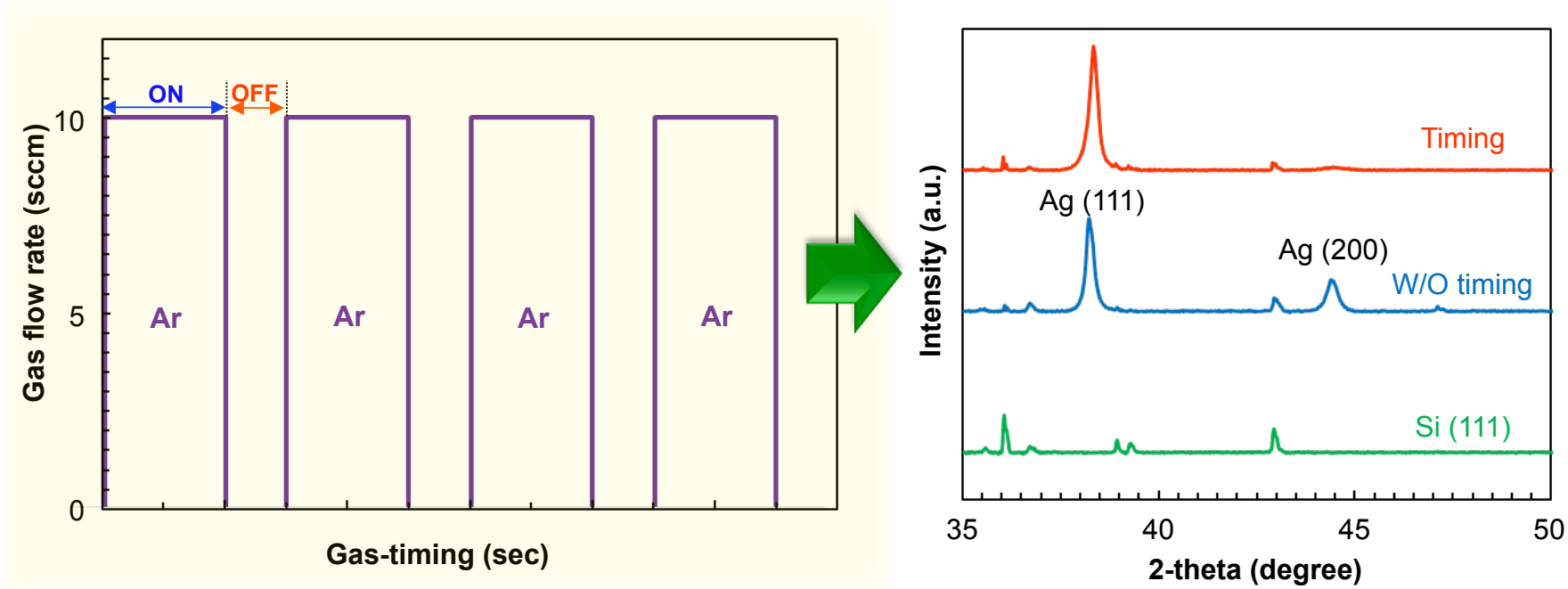
-Advantages-

- Large area coting 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-

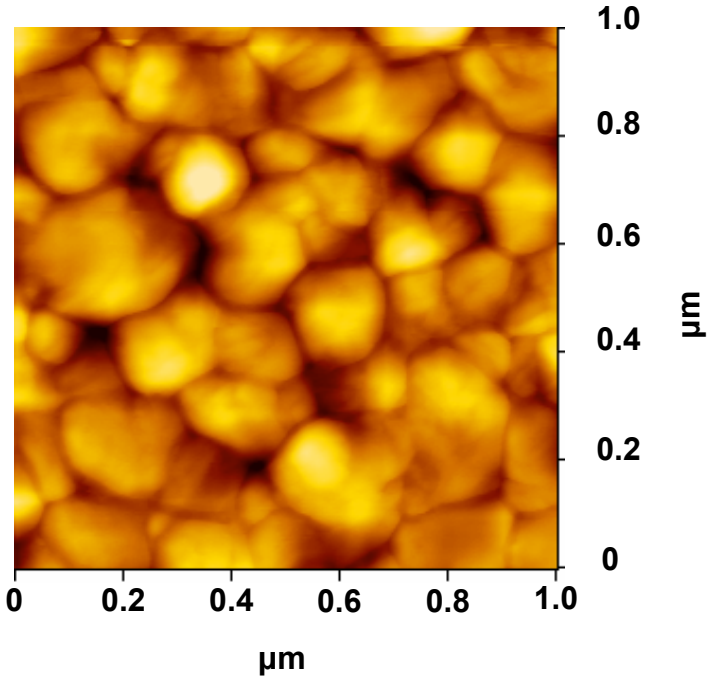


High order texture of Ag (111) thin films could be fabricated by using gas-timing rf magnetron sputtering technique

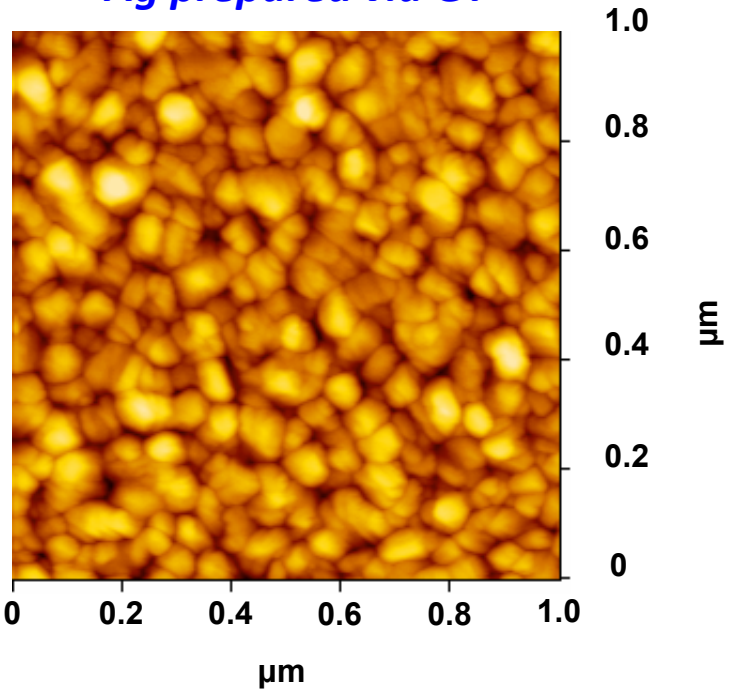
Can we control structure and morphology of Ag thin films via GT technique?

-Morphology-

-Ag prepared via w/o GT-

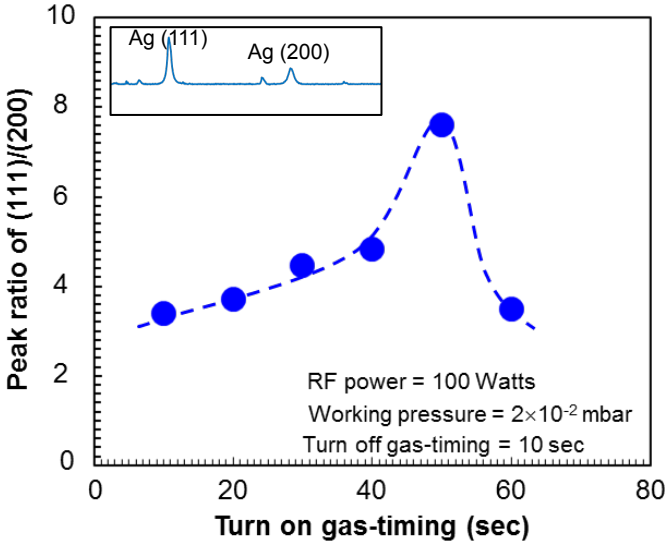


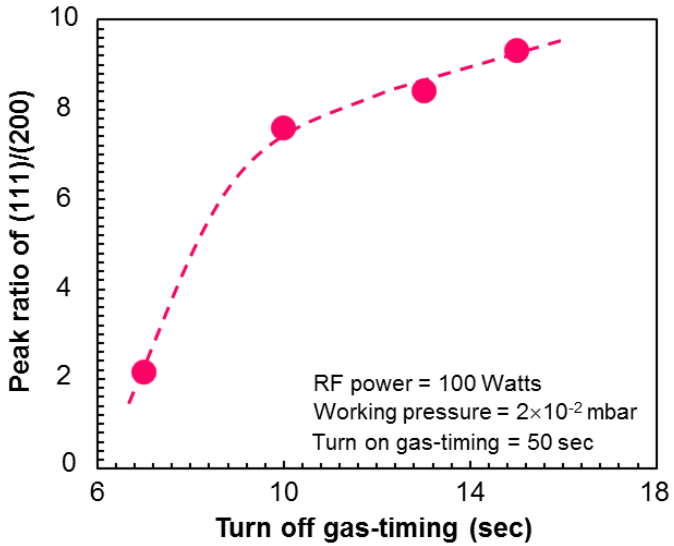
-Ag prepared via GT-

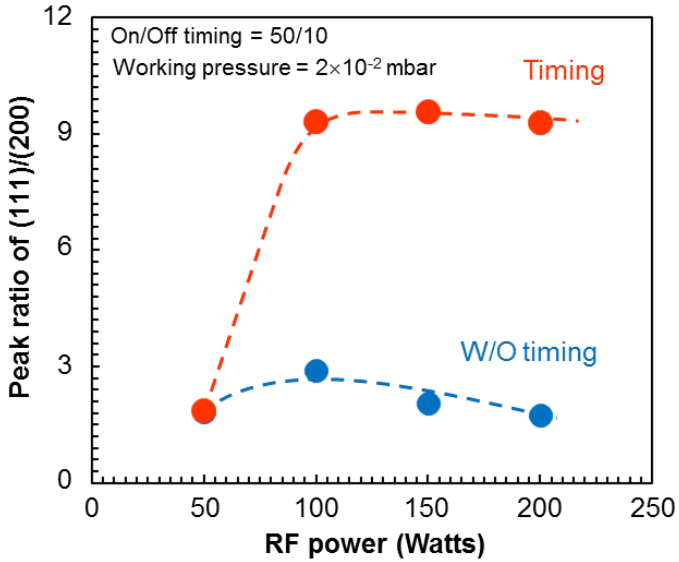


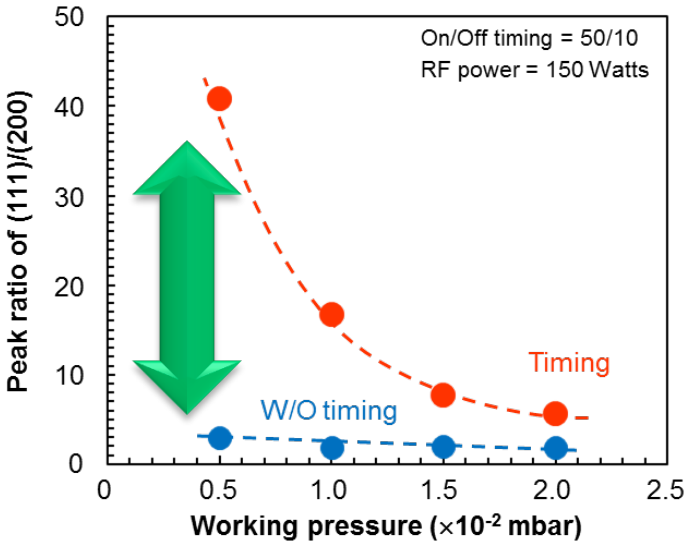
Smaller grain size could be obtain when GT technique is utilized

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



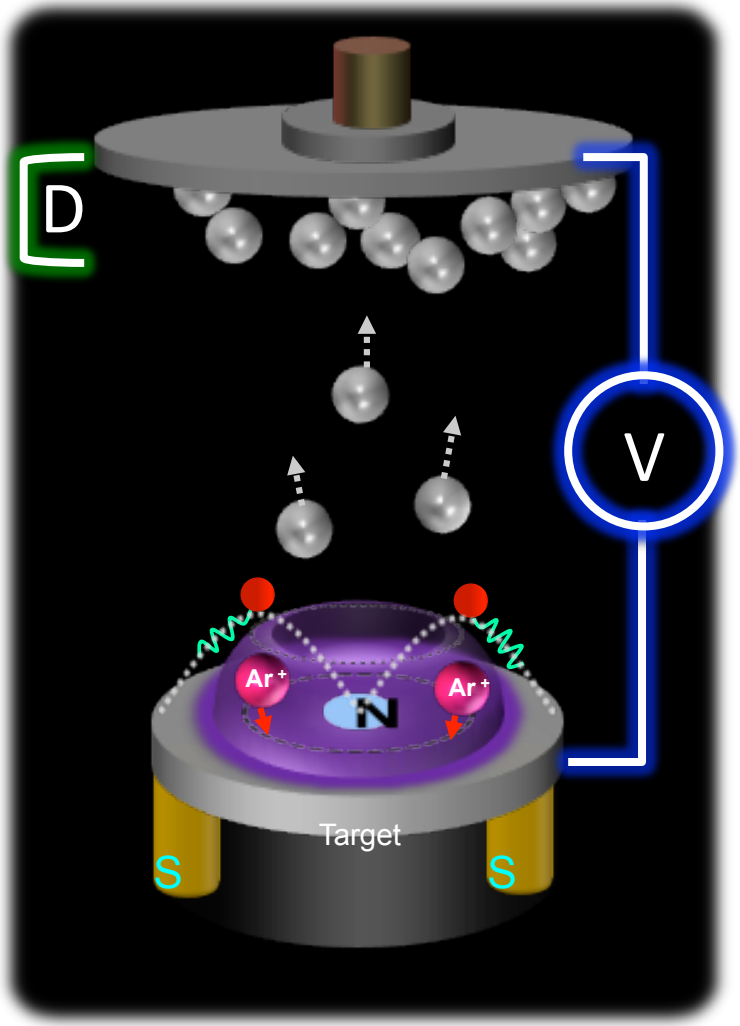




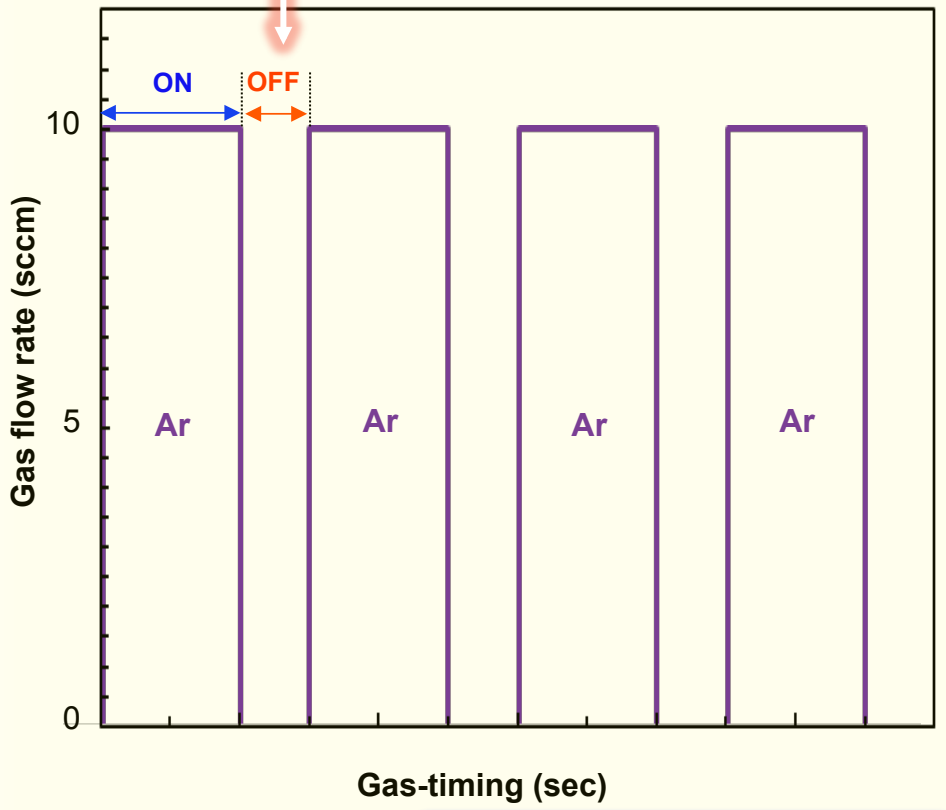


How does gas-timing technique enhance the crystal growth?

How does gas-timing technique enhance the crystal growth?



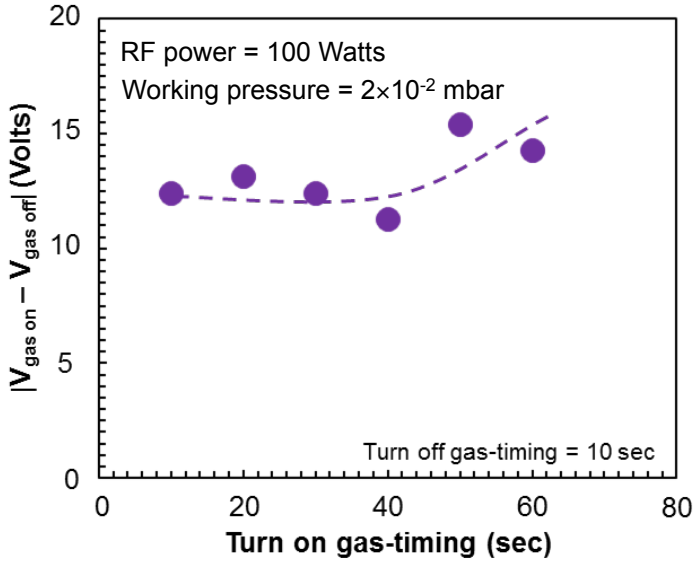
Lower sputtered atom with constant sputter energy

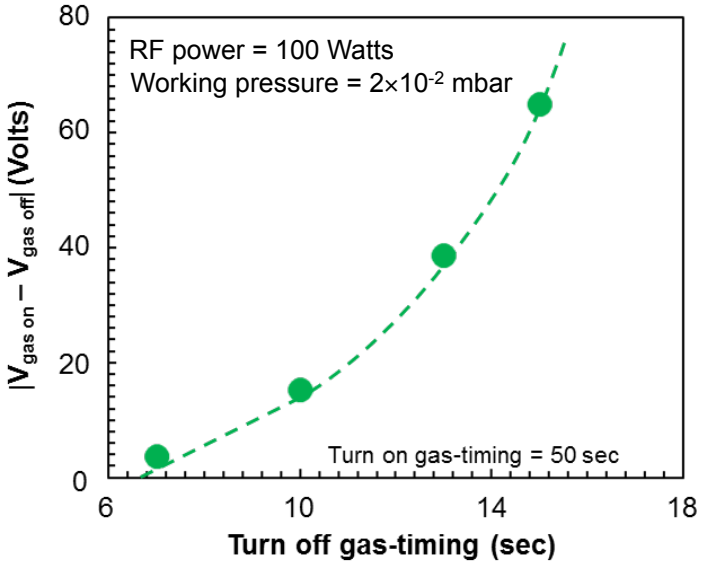


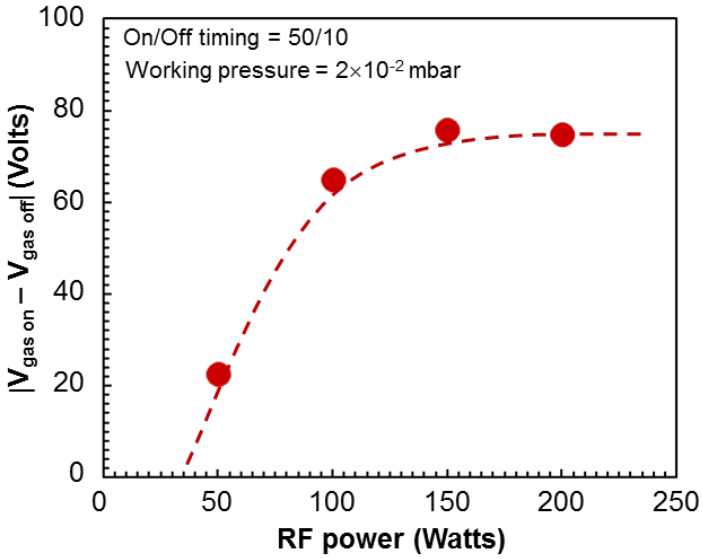
$$\text{Energy per atom} = \frac{\text{Total sputtered energy}}{\text{Total sputter gas atom}}$$

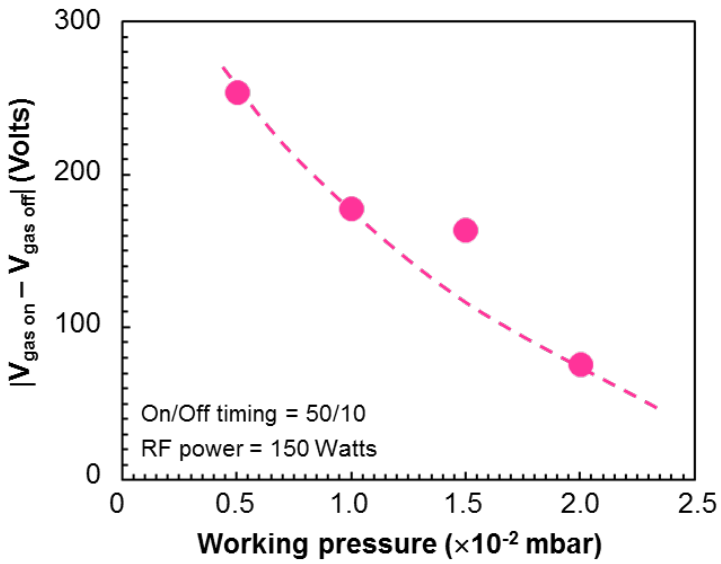
Higher energy of sputtered atoms might be raised during turn-off sequence.

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



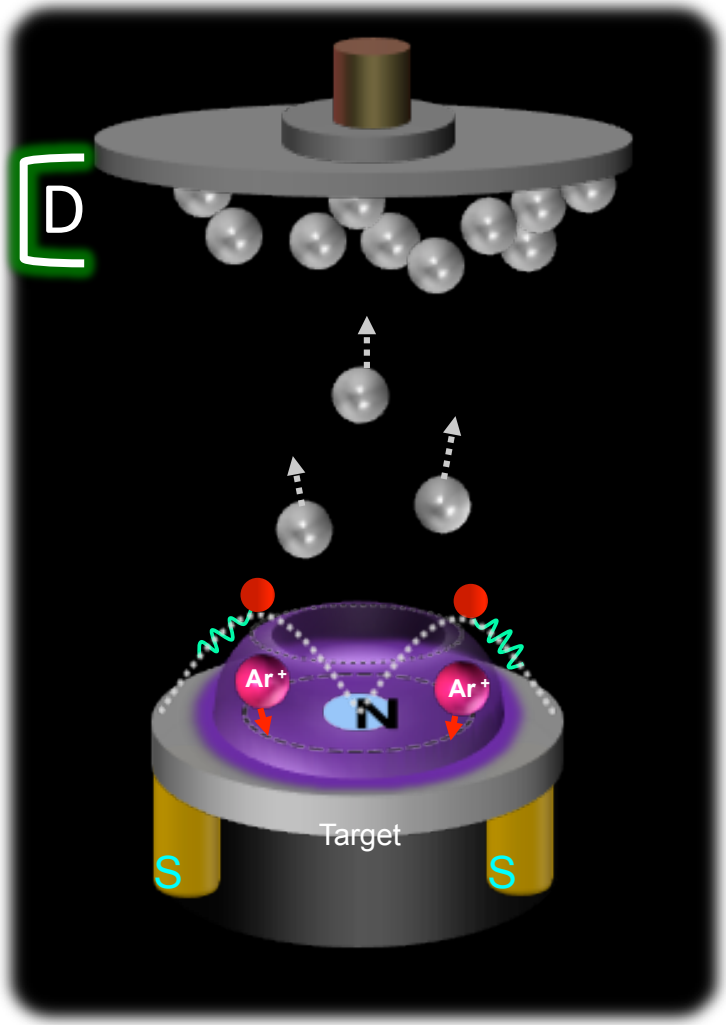




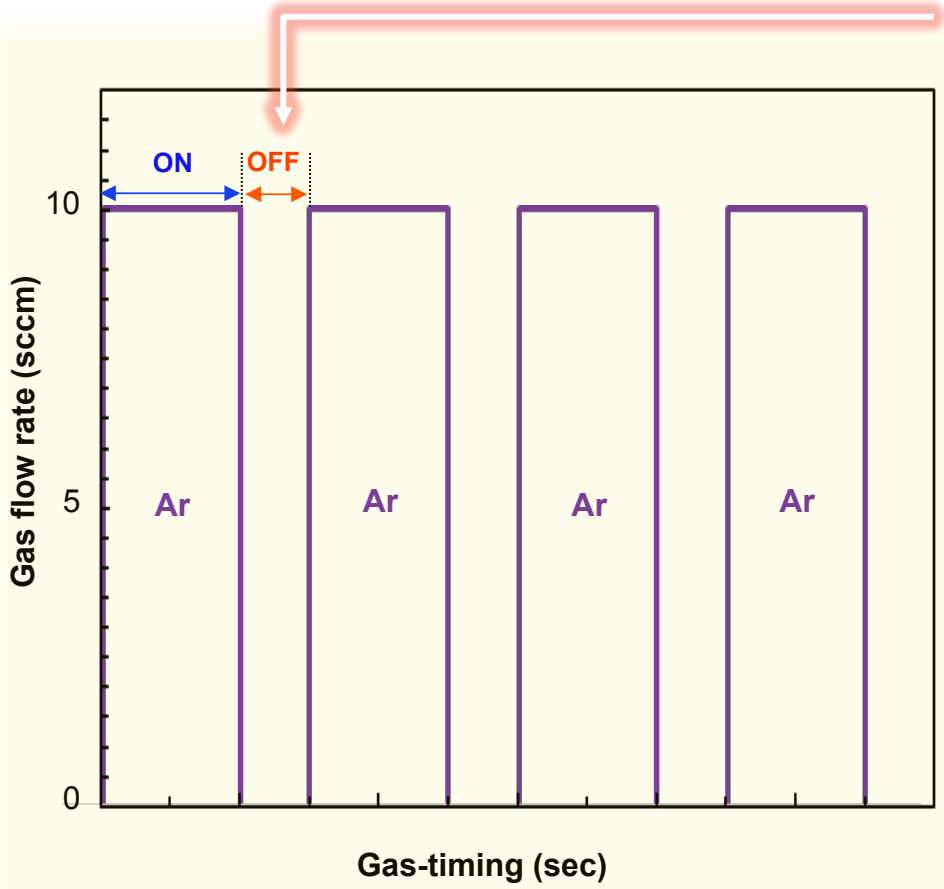


Gas-timing technique strongly enhanced the total sputtered energy

How does gas-timing technique enhance the crystal growth?



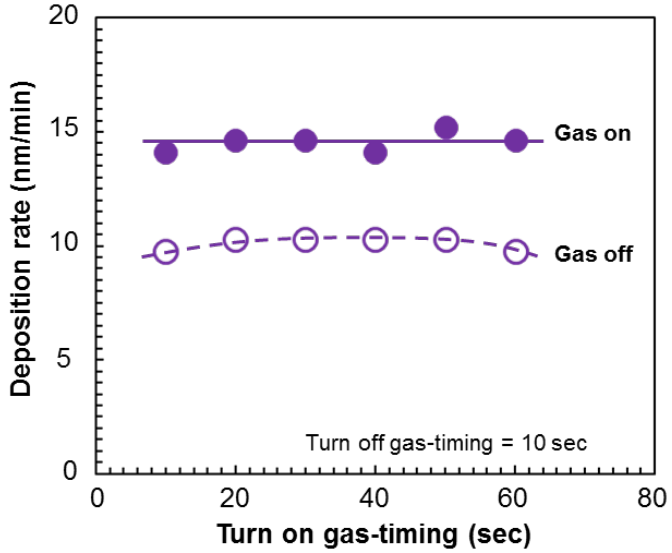
Lower sputtered atom with constant sputter energy

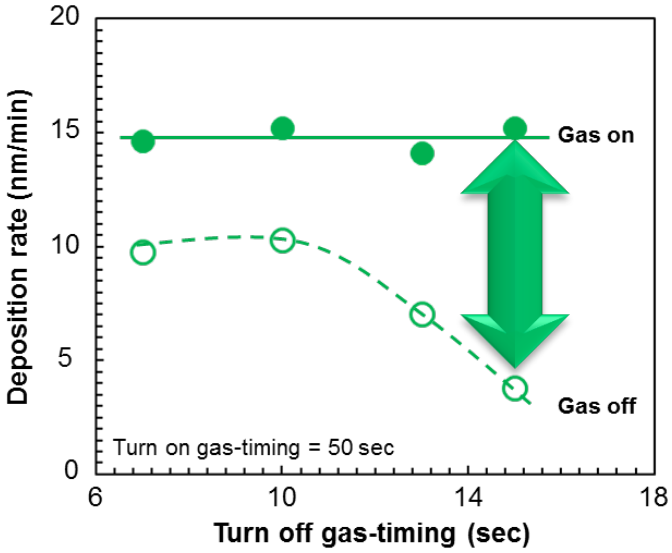


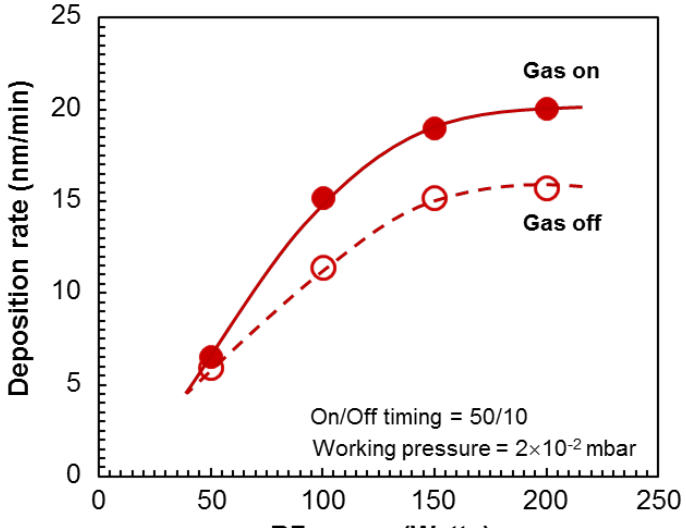
Energy per atom = Total sputtered energy / Total sputter gas atom

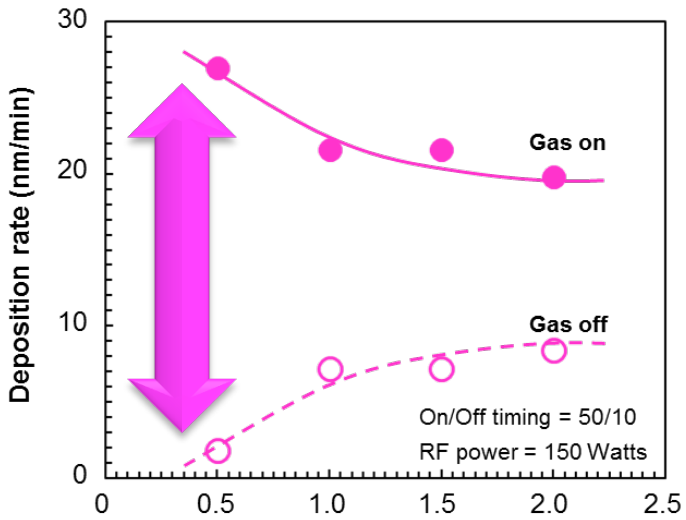
Higher energy of sputtered atoms might be raised during turn-off sequence.

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

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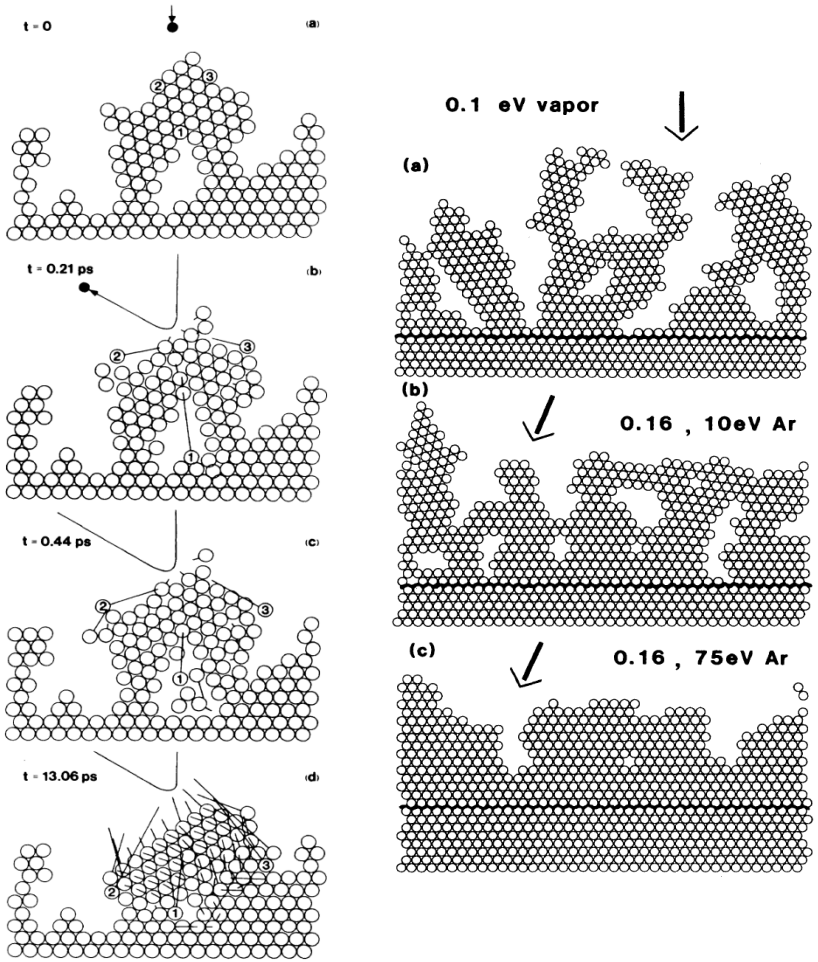
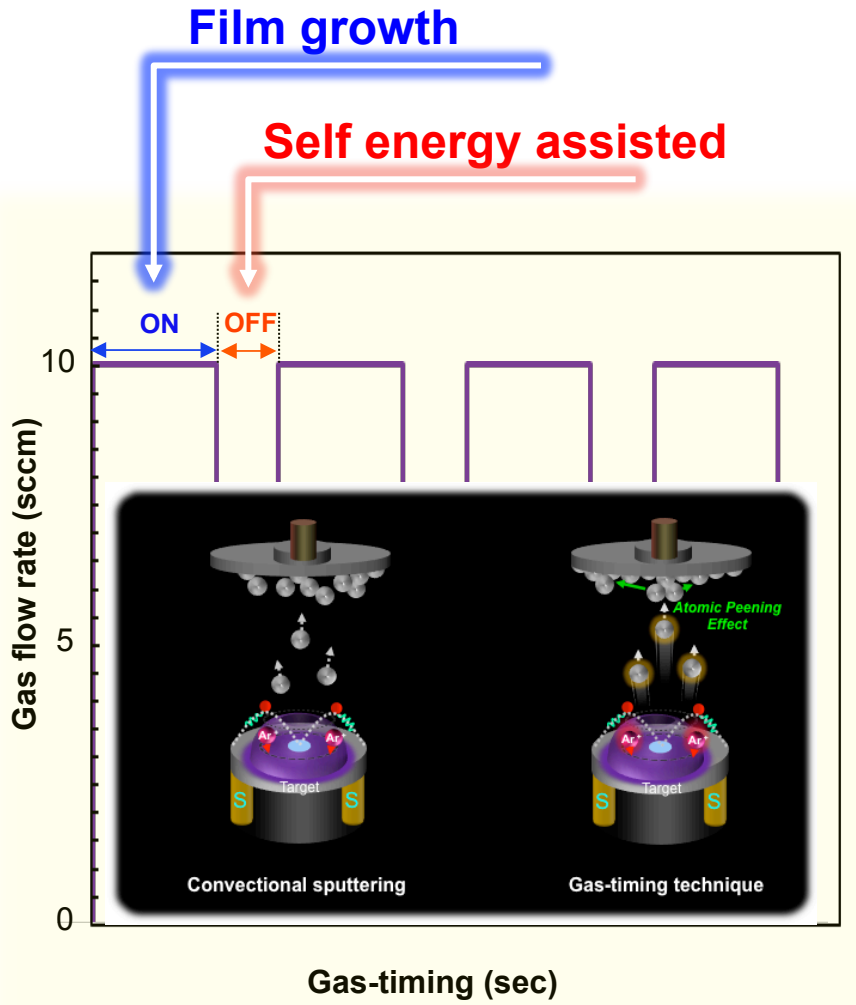
(Received 5 May 1986; revised manuscript received 24 December 1986)

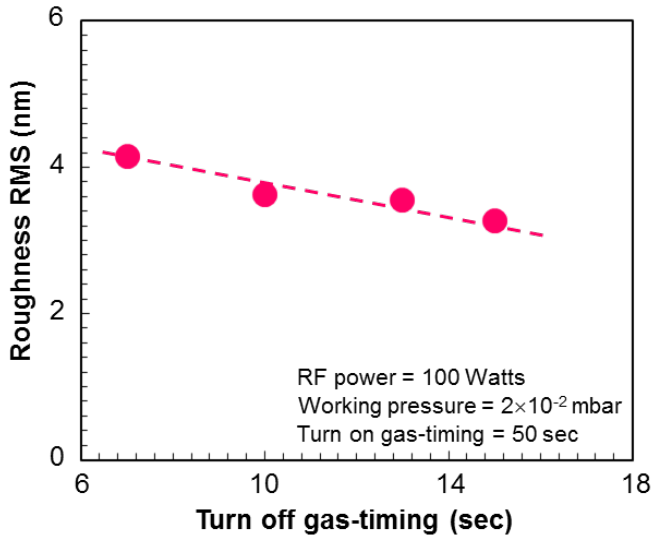


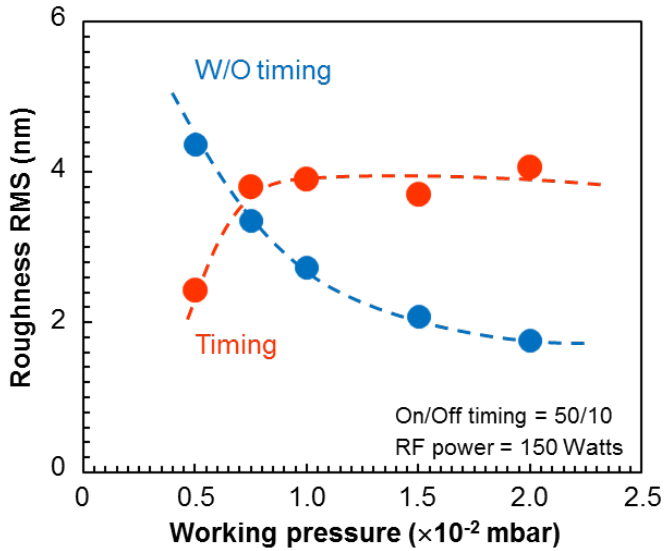


Self energy assisted might be provided by gas-timing technique

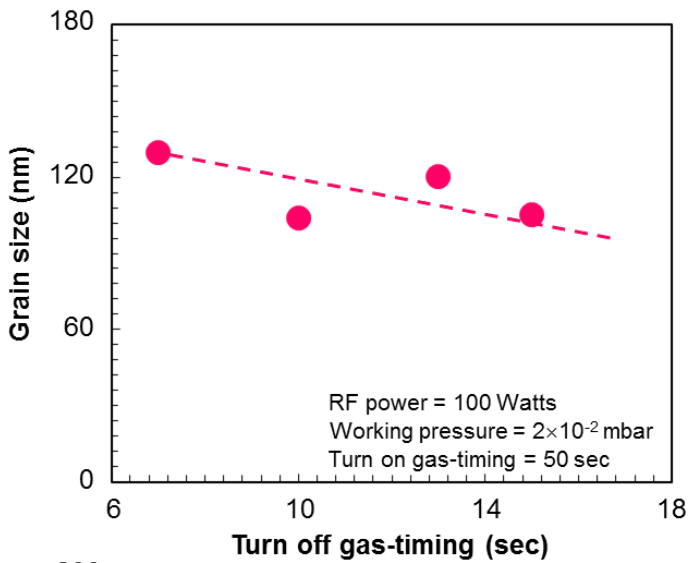
Morphology of Ag thin films

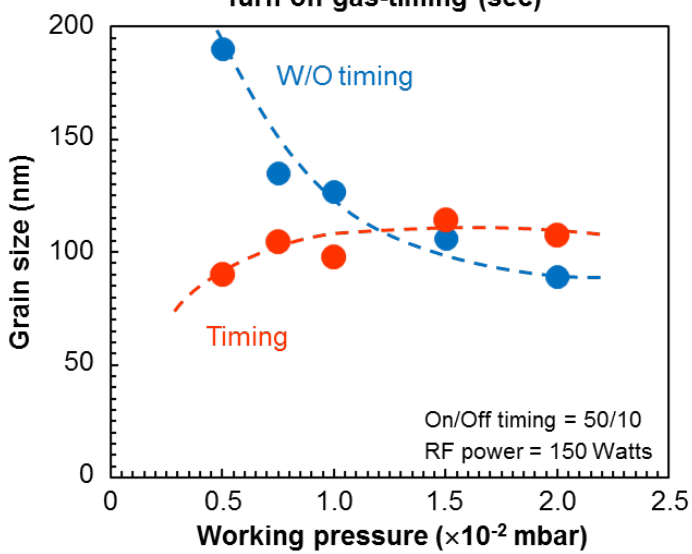
-Roughness RMS-





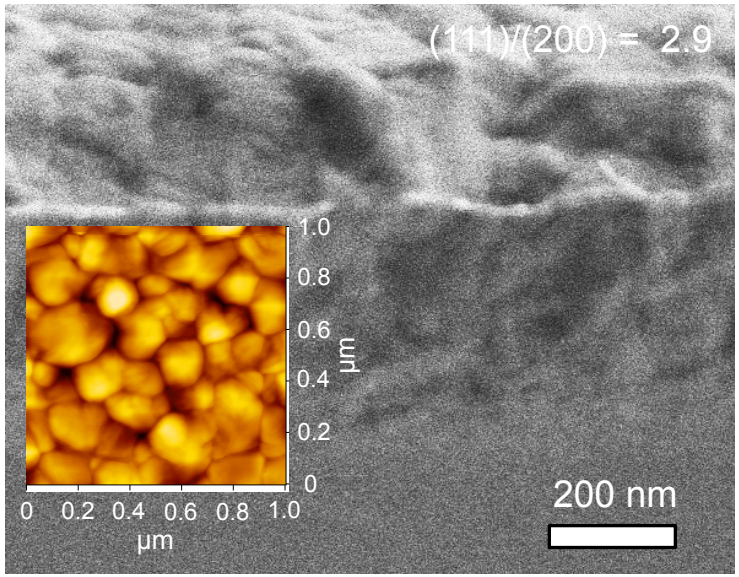
-Grain size-

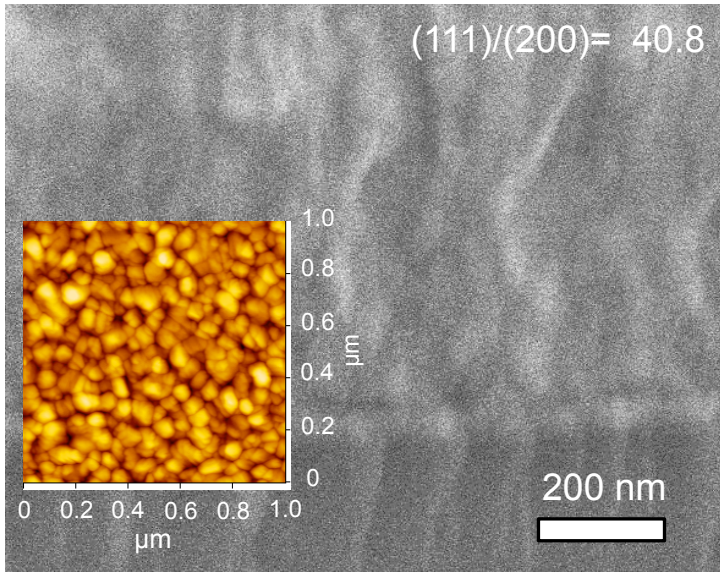


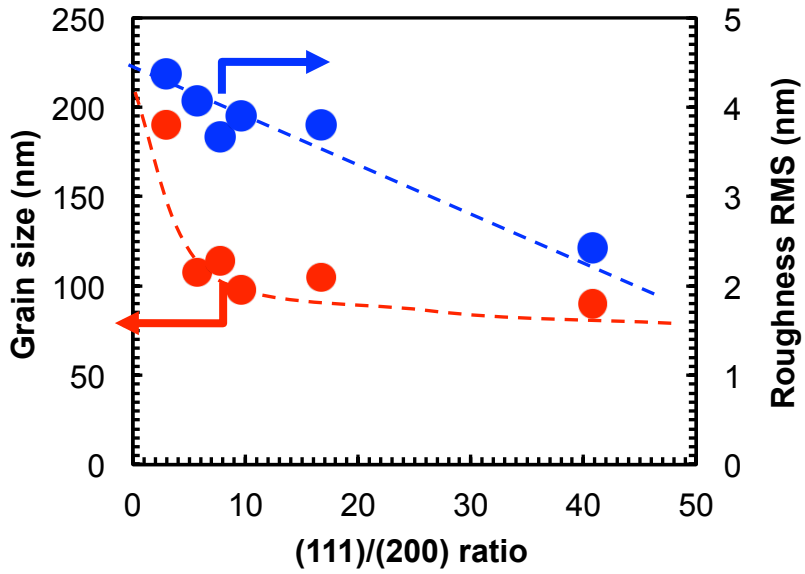


Dense structure of Ag (111) might be obtained via adatom diffusion via high energy during sputter deposition

Morphology vs. Texture oreintation







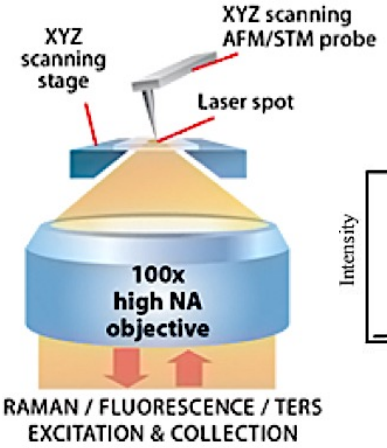
Controllability on texture orientation and morphology can be archived via GT technique

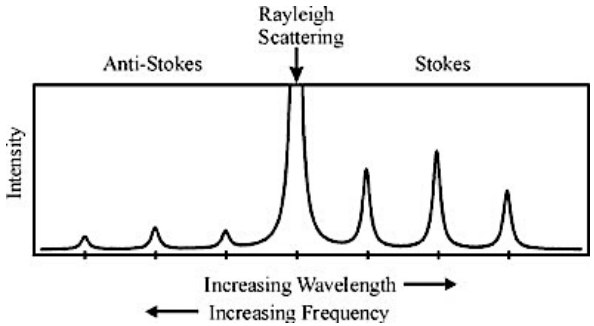
SERS Measurement

-NT-MDT NTEGRA SPECTRA-

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

Reflection Mode

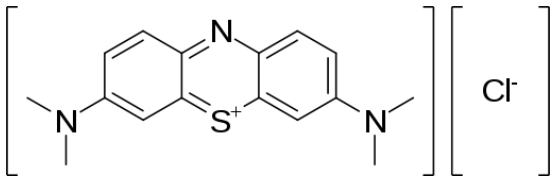




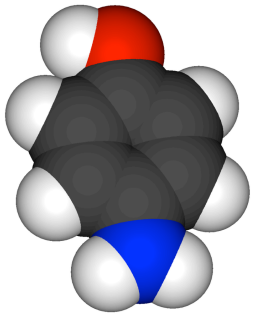
-Raman Active Molecule-

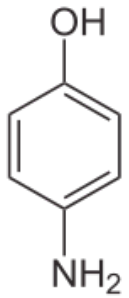
Methylene Blue (MB)

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



4-Aminophenol

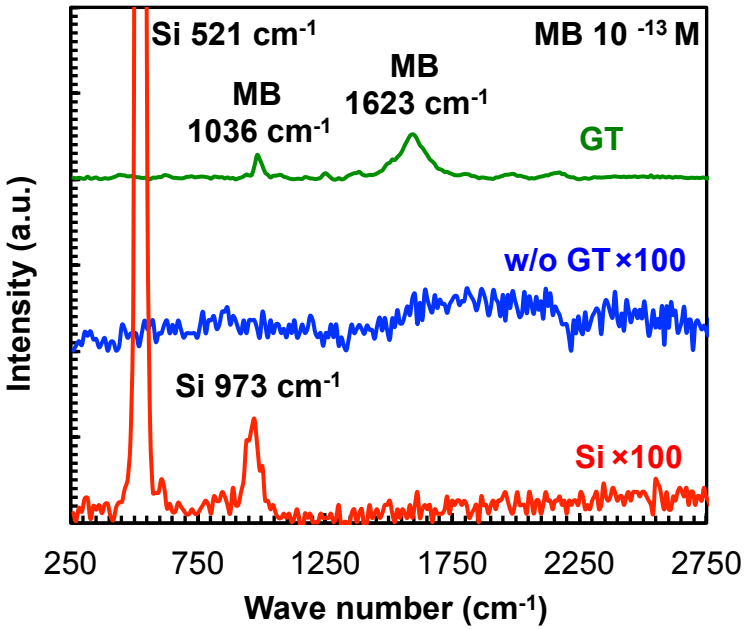




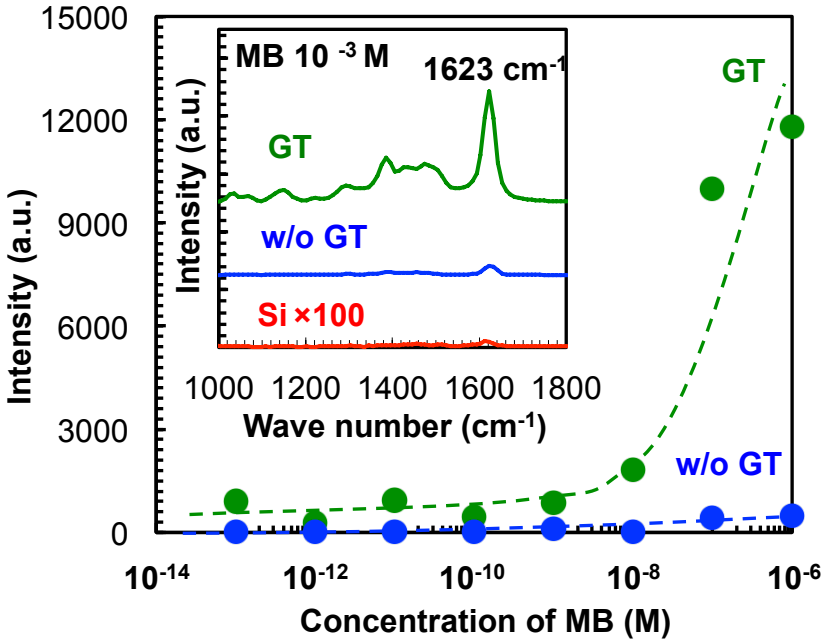
10^{-3} to 10^{-12} M

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 cm^{1}-



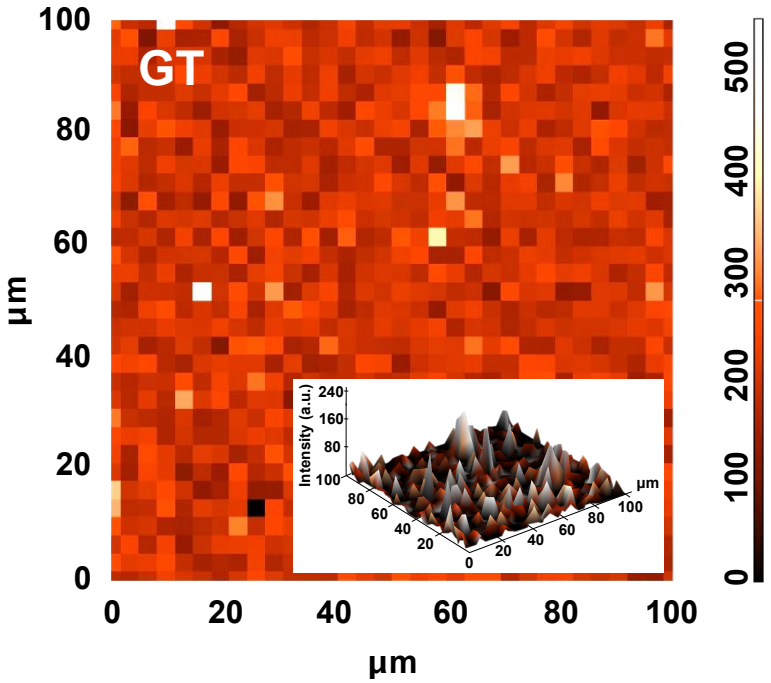
-Morphology of Ag thin films-

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

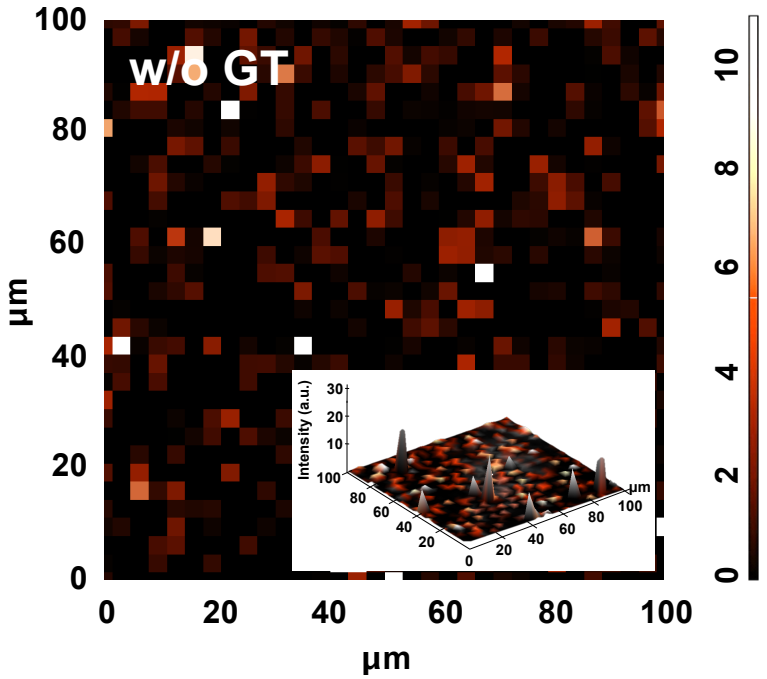
High sensitivity SERS substrate is successfully fabricated via GT technique

SERS mapping: Distribution of SERS signal

-SERS Mapping of GT substrate-



-SERS Mapping of Conventional substrate-



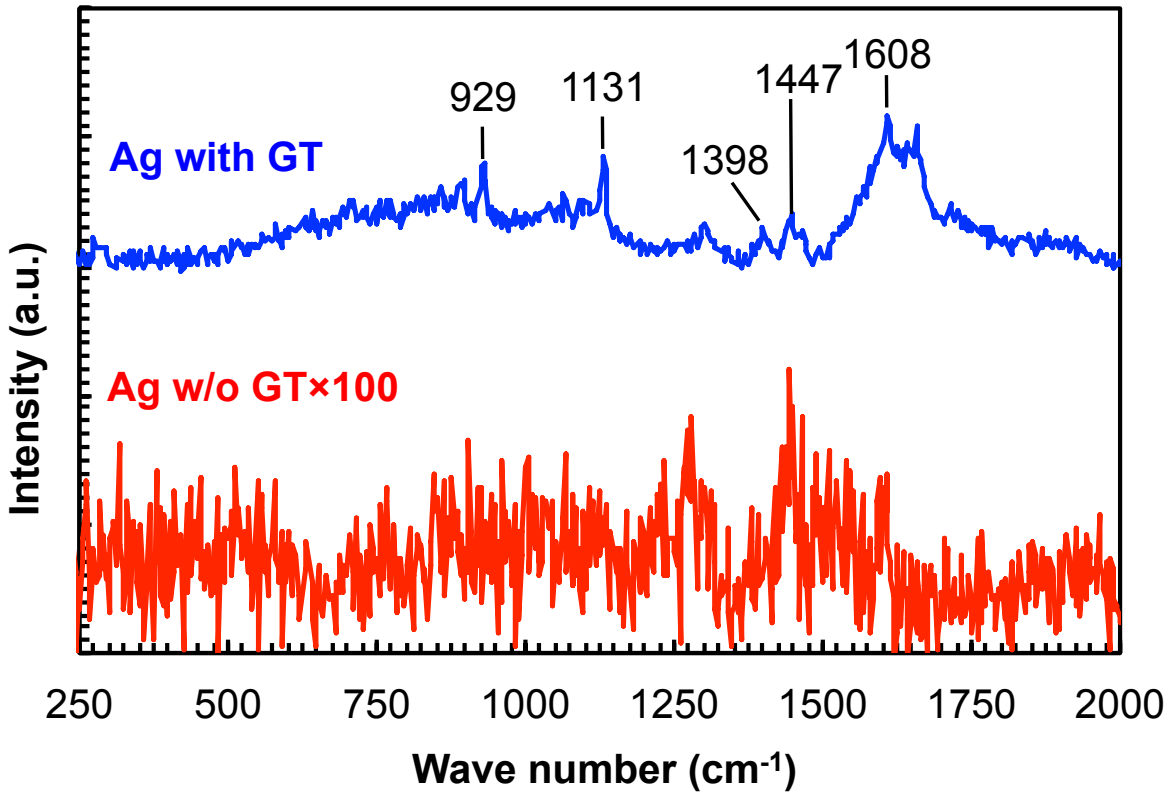
$$\mathrm{EF} = \frac{I_{\mathrm{SERS}}}{I_{\mathrm{Ref}}} \frac{N_{\mathrm{Ref}}}{N_{\mathrm{SERS}}}$$

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

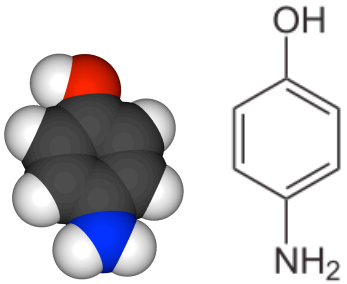
Uniformity of SERS signals can be accomplished when the SERS substrate fabricated by the GT technique is utilized.

Are we confident with our SERS substrate?

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



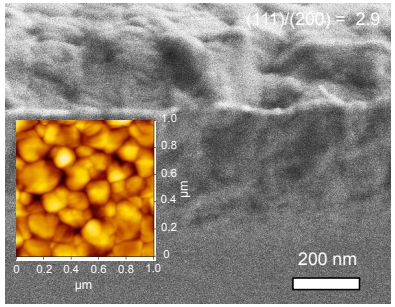
-4-Aminophenol-

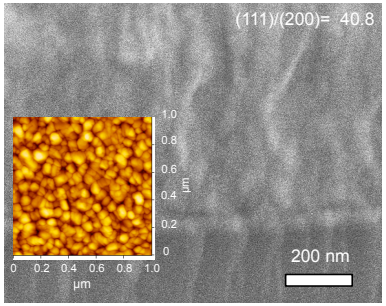


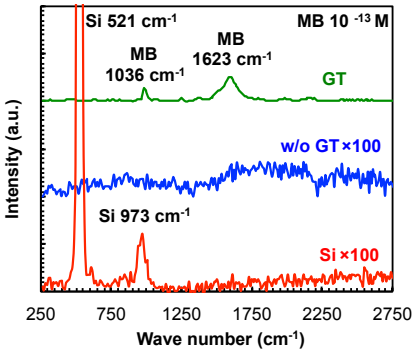
Ag thin films prepared by GT technique are promising for SERS activities

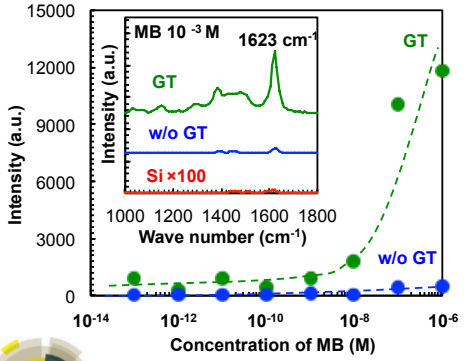
Summary

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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สวทช NSTDA

Thank you very much for your attention