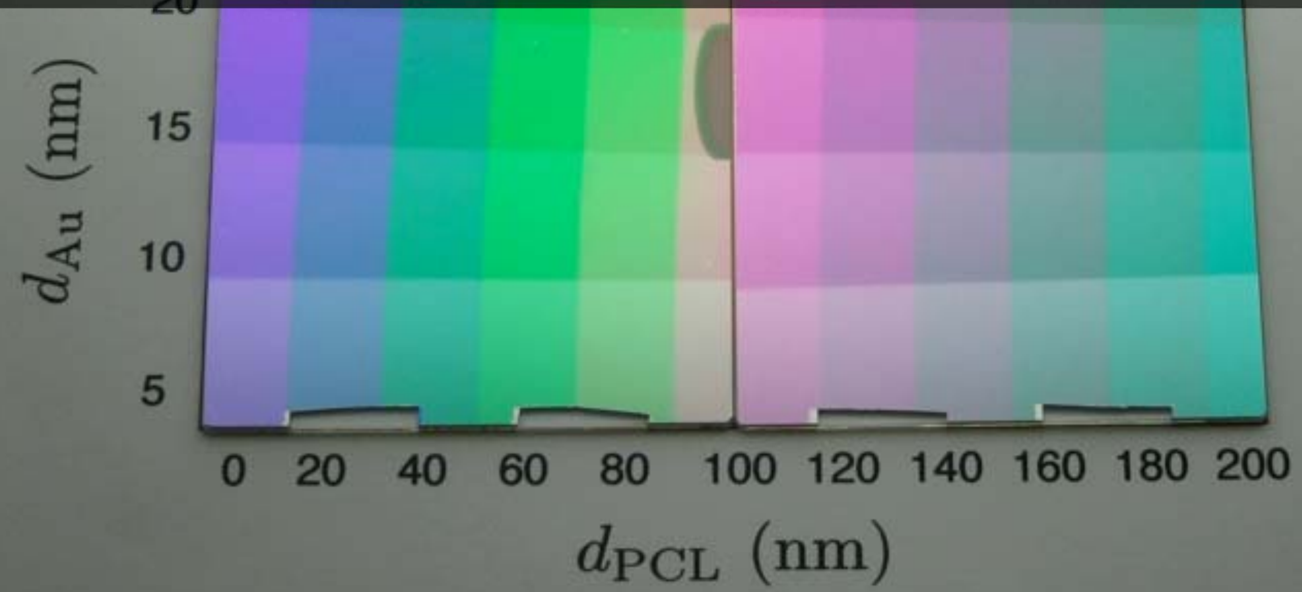
物理的自己組織化による薄膜のナノ形態制御と応用

― SERS，光学素子，MEMSへの展開 ―

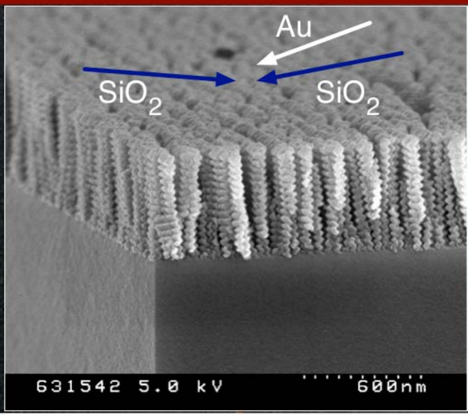


鈴木 基史

京都大学

Progress of our research on nanoparticles

Au, Ag nanorod arrays



M. Suzuki *et al.*, "Direct formation of arrays of prolate Ag nanoparticles by dynamic oblique deposition," Jpn. J. Appl. Phys. Part 2 **44** (1-7), L193-L195 (2005).

SERS & PC-SERS

M. Suzuki *et al.*, "In-line aligned and bottom-up Ag nanorods for surface-enhanced Raman spectroscopy," Appl. Phys. Lett. **88** (20), 203121 (2006).

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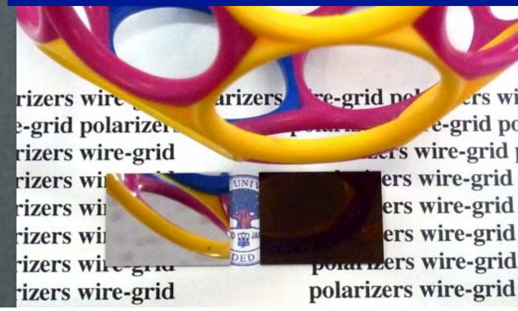
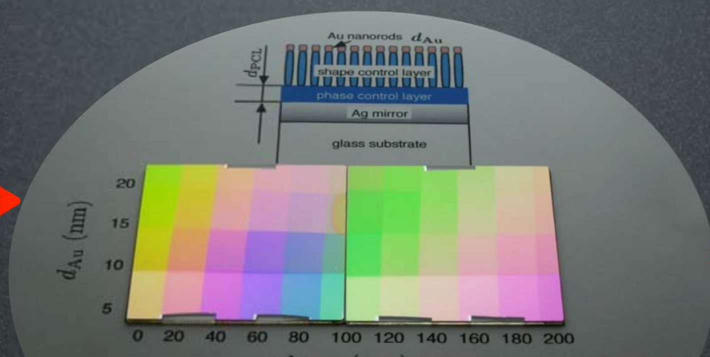
Polarizer

LR-WG polarizers



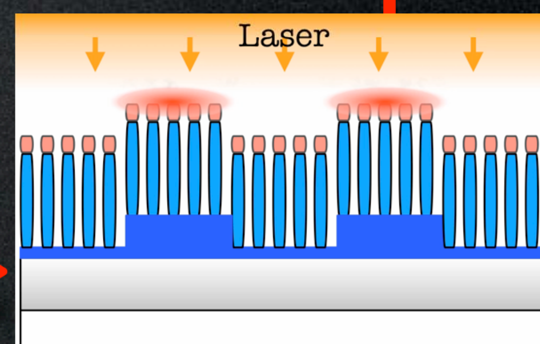
M. Suzuki *et al.*, "Low-reflective wire-grid polarizers with absorptive interference overlayers," Nanotechnology **21** (17), 175604 (2010).



Local plasmon resonator for SERS

M. Suzuki *et al.*, "Tailoring coupling of light to local plasmons by using Ag nanorods/structured dielectric/mirror sandwiches," Journal of Nanophotonics **3** (1), 031502 (2009).

- Photothermal devices for micro-fluid?
- Polarized & Wavelength selective IR emitters?



Spatiotemporal nanoheaters

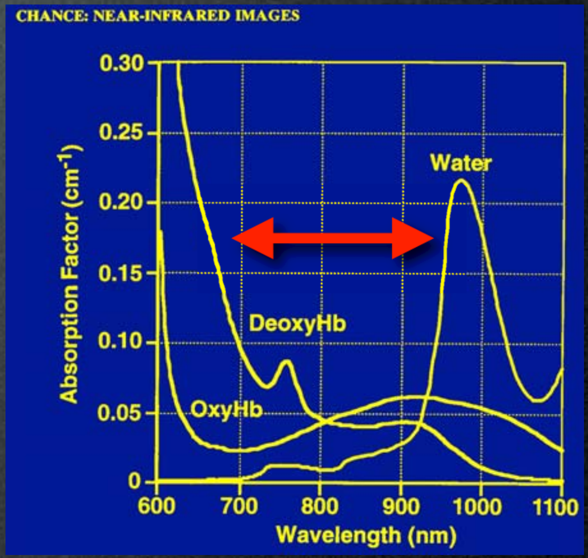
- Nanoparticle absorber
  - Enhanced properties
  - New functions

Au nanorod arrays for SERS

In-line aligned Au nanorods prepared by dynamic oblique deposition (DOD)

Near-IR Surface Enhanced Raman Scattering (SERS)

- SERS: Direct and sensitive method to identify molecules
  - Drastic enhancement of the local field due to plasma resonance in metal nanoparticles
- Why NIR?
  - Compatible with a biological tissues' transparency window
    →little damage to tissues

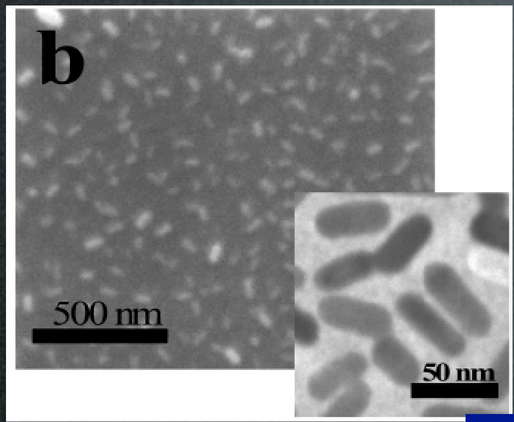


[1] B. Chance, "Near-Infrared Images Using Continuous, Phase-Modulated, and Pulsed Light with Quantitation of Blood and Blood Oxygenation," Annals of the New York Academy of Sciences **838**, 29-45 (1998).

In order to develop the NIR SERS substrates, control of size, shape and arrangement of nanoparticles are important!

Various 'nanorods' for NIR SERS substrates

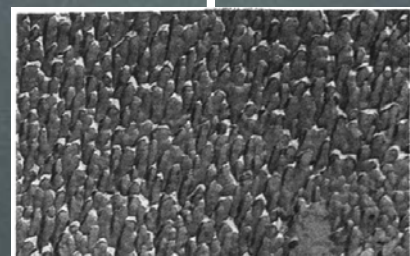
Orendorff et al., Anal. Chem. 77, (2005) 3261.
Random aggregates of nanorods



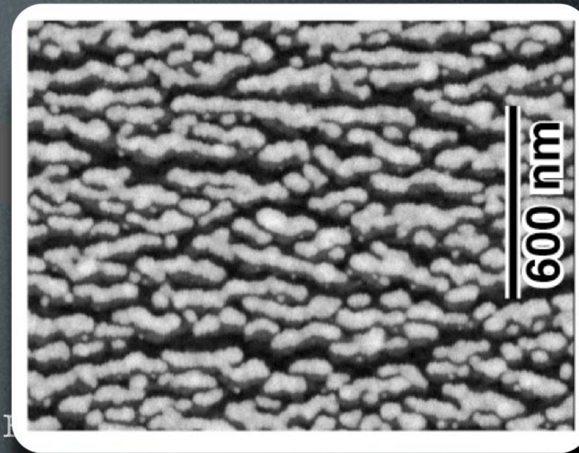
bottom up

Low cost

Martínes et al., Phys. Rev. B 35 (1987) 9481.
Obliquely deposited columns.

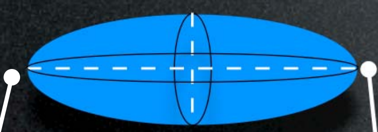


M. Suzuki et al., Jpn. J. Appl. Phys., **44**, L193-L195 (2005).



random

- We have succeeded in aligning the nanorods end-to-end.
  - Physical self-assemble technique: Dynamic oblique deposition.

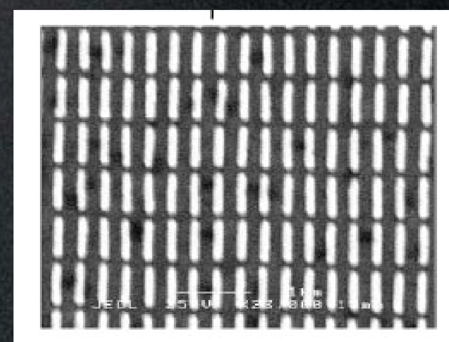


Local field can be significantly enhanced at the end of nanorod.

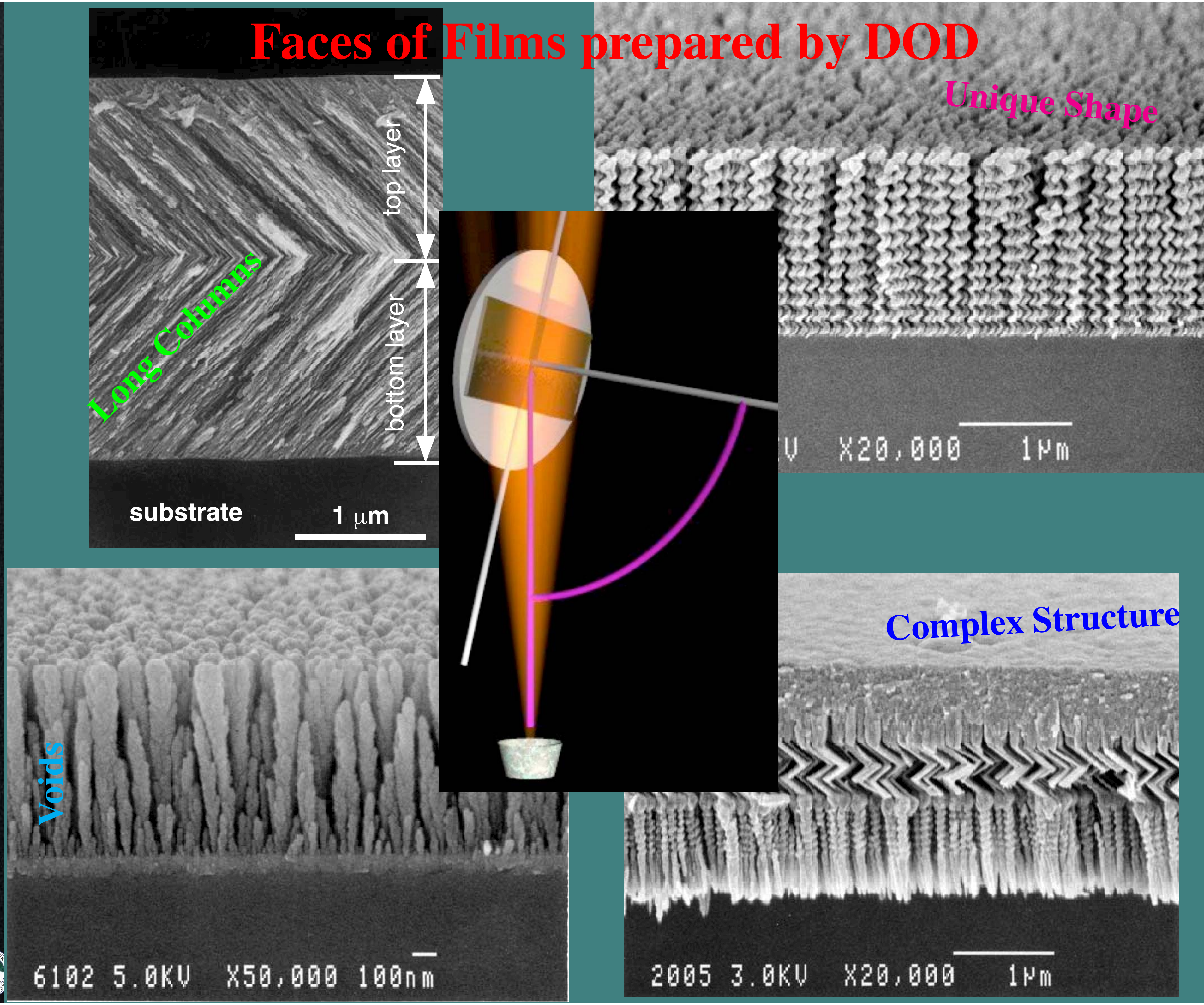
Further enhancement is expected for in-line alignment.

top down

Expensive

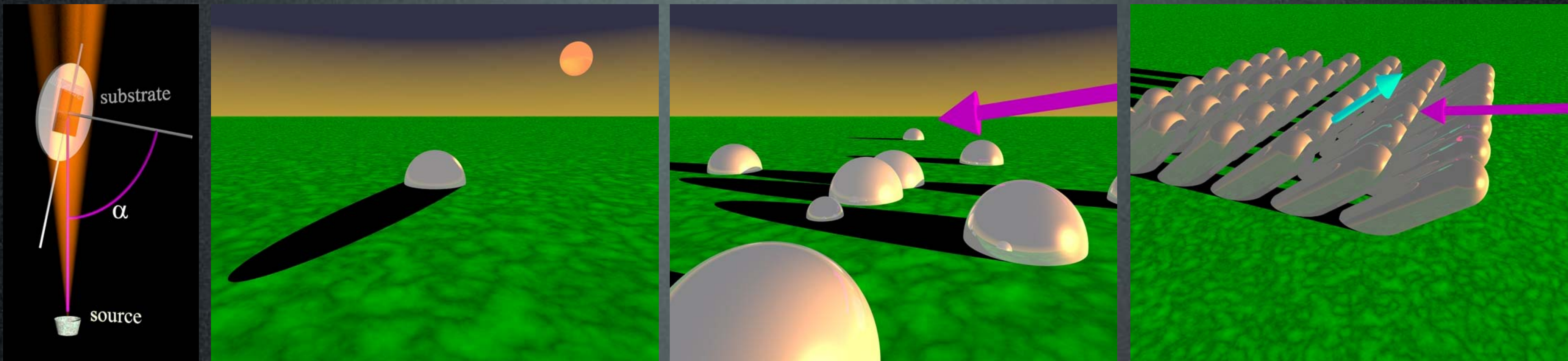


Faces of Films prepared by DOD



友会館

Growth mechanism of oblique columnar structure



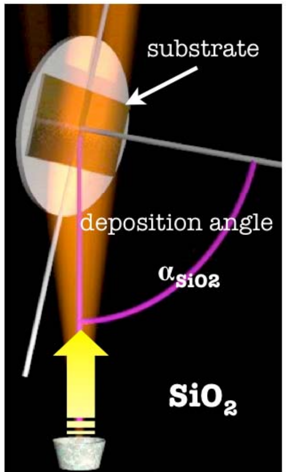
Nucleation | Self-shadowing | Columnar growth

- The physical origins of the columnar structure in obliquely deposited thin films are the self-shadowing effects and the limited mobility of the deposited atoms.
  - When the vapor flux is obliquely incident, atoms in the growing films shadow unoccupied sites from the direct sticking of incident atoms.
  - Owing to limited mobility, the unoccupied sites are not filled later. → Large islands grow selectively.
  - Oblique columns grow in the direction of the incident vapor beam.

Preparation of shape control layer

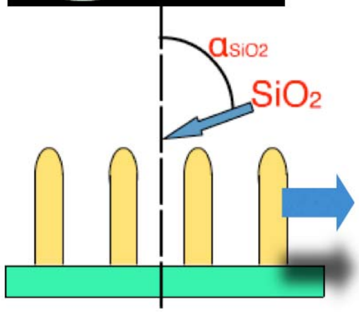
① Preparation of SiO_2 template

(Serial bideposition[SBD])



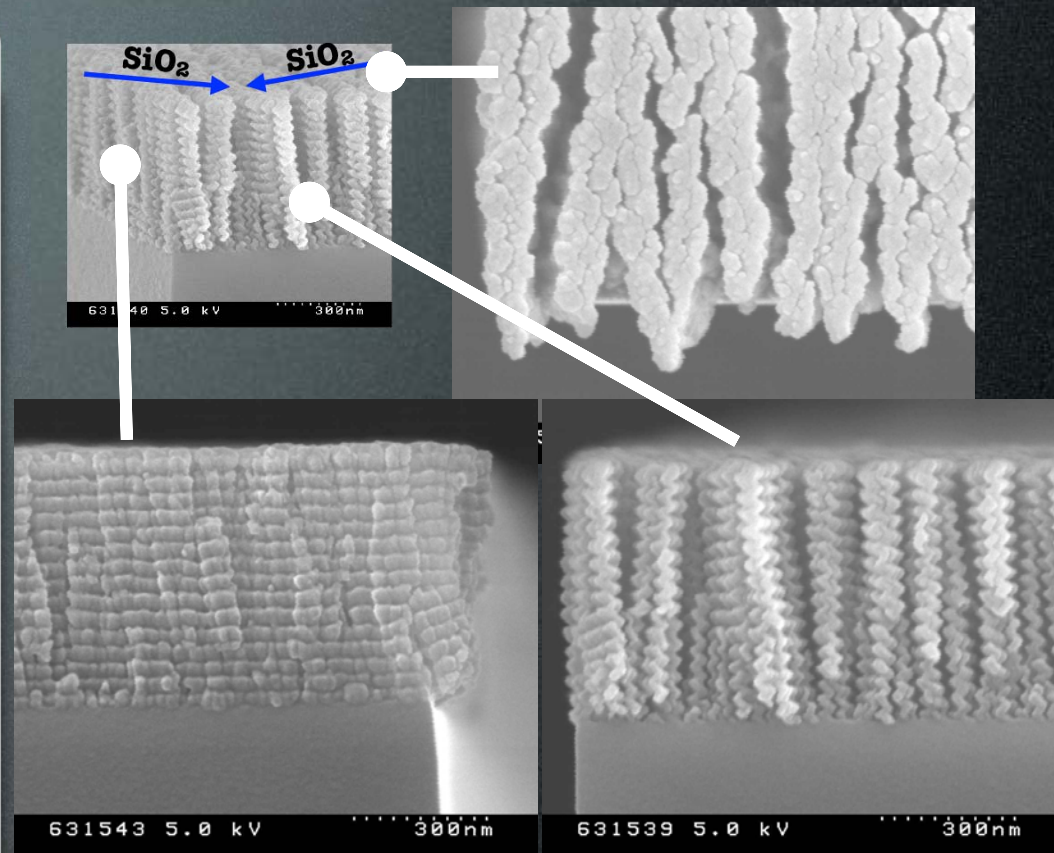
Substrate: Ordinary flat glass

Substrate is set at oblique angle and rotated by 180° with each deposition of 10 nm thick.



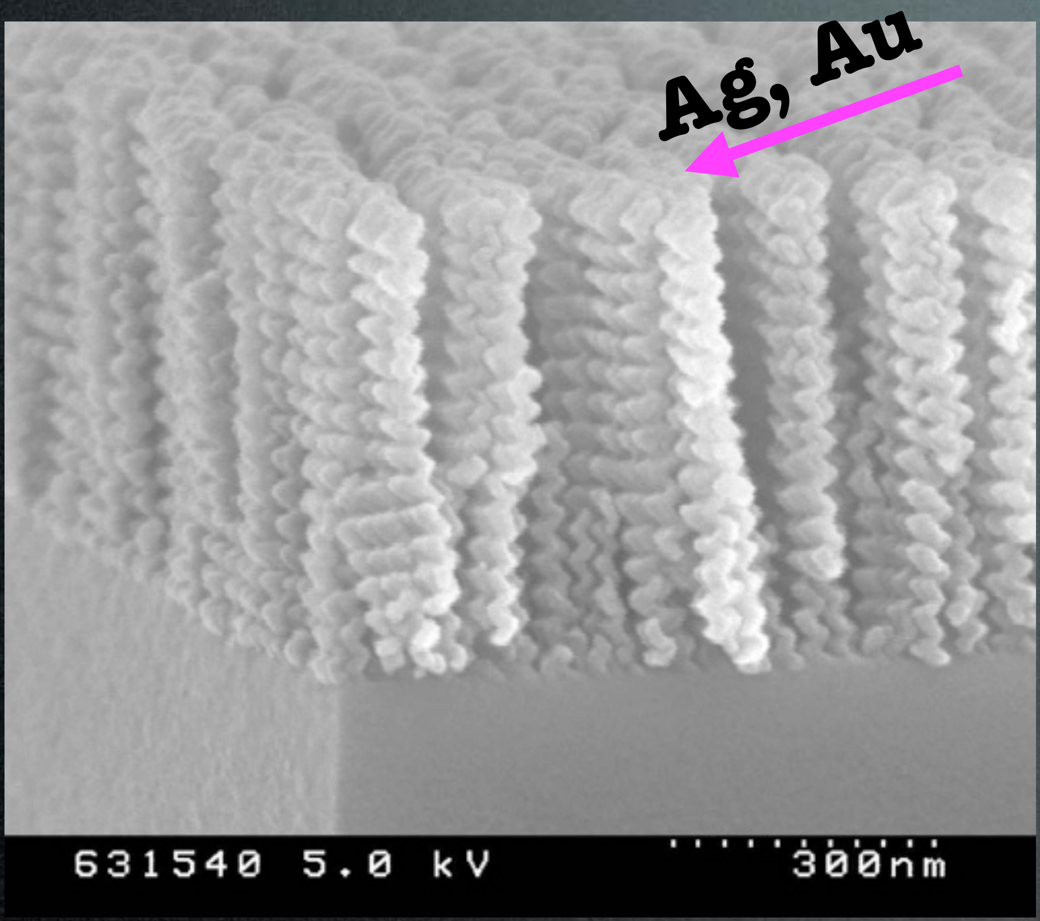
$\alpha_{SiO2} \rightarrow 79°$

$d_{SiO2} \rightarrow 0 - 500$ nm

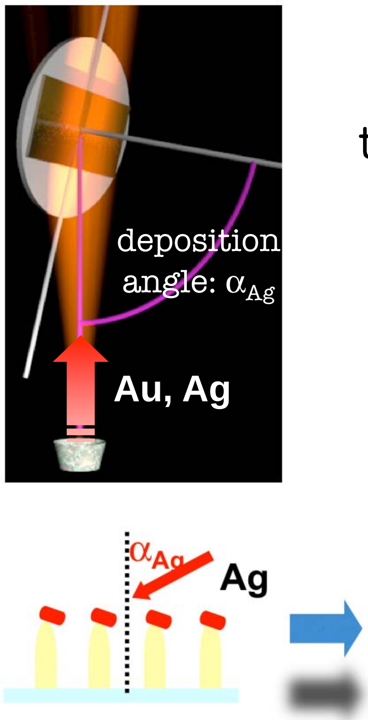


- Columnar morphology characteristic to serial bideposition is physically self-assembled.

Preparation of nanorod arrays by DOD



② Oblique deposition of Ag (or Au)



thickness of Au, Ag ;

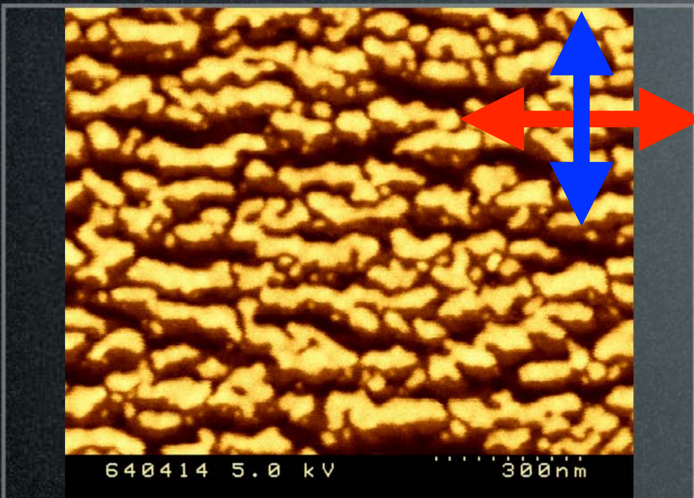
$d_{\mathrm{Au,\,Ag}}$

$\alpha_{\mathrm{Au,\,Ag}} \rightarrow 73^\circ$

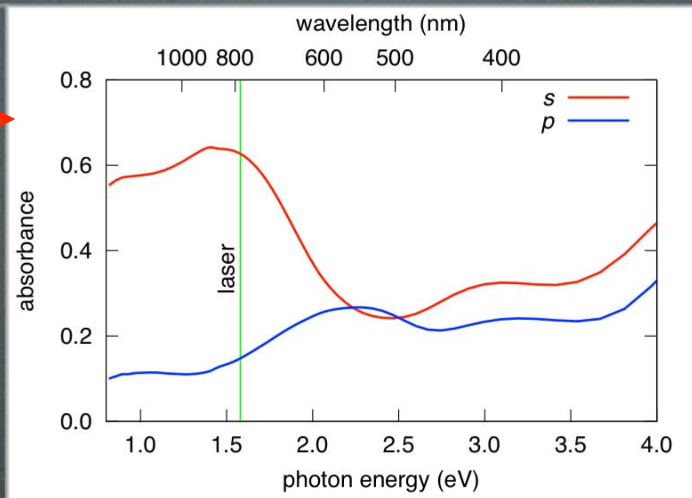
$d_{\mathrm{Au,\,Ag}} \rightarrow 1\sim25$ nm

- Au, Ag sticks only to the top of columns due to the self-shadowing and forms elongated nanoparticles so-called nanorods.

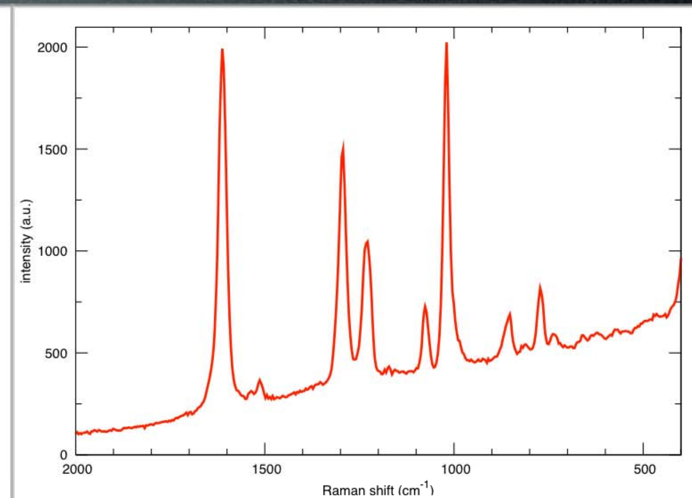
Properties of Au nanorod arrays $(t_{\mathrm{Au}} = 10\ \mathrm{nm},\ \alpha_{\mathrm{Au}} = 73^\circ)$



SEM of Au nanorods.

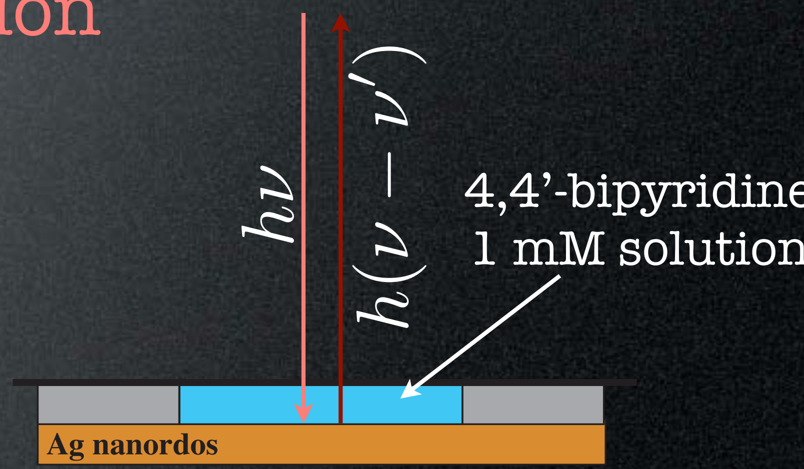


Absorbance spectra.



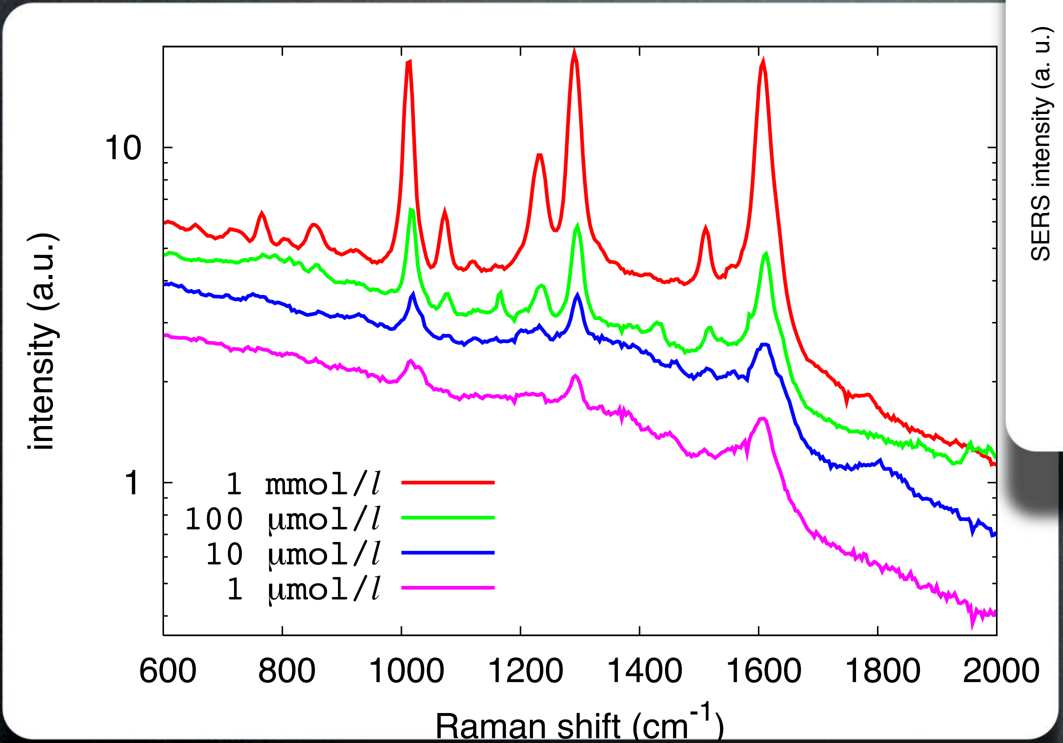
SERS spectra of 4,4'-bpy solutions measured on Au NRA. (λ=785 nm)

- In-line aligned nanorods
  - Polarization dependent absorption due to local plasma resonance.
  - Strong SERS. ~10^7 times enhancement

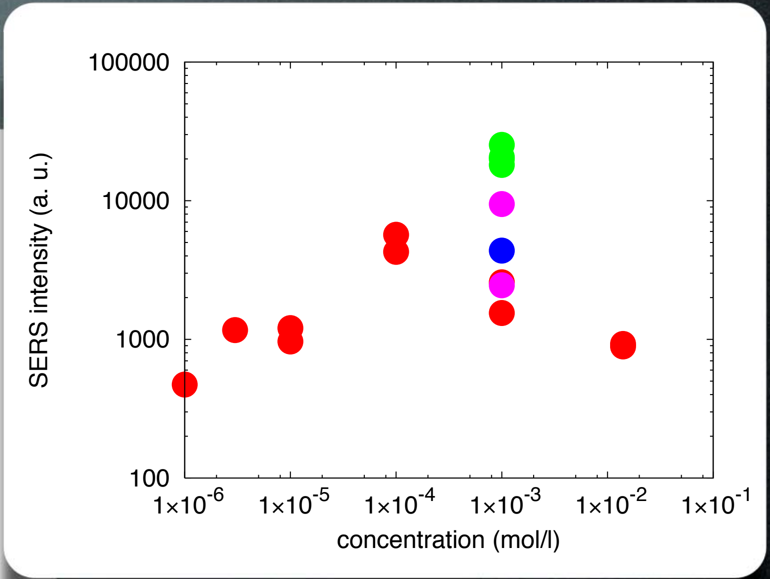


[1] M. Suzuki, K. Nakajima, K. Kimura, T. Fukuoka, and Y. Mori, "Au Nanorod Arrays Tailored for Surface-Enhanced Raman Spectroscopy," Analytical Sciences **23** (7), 829-833 (2007).

SERS強度の濃度依存



SERSスペクトルの変化 (〜15 mW)



1014 cm^{-1}近傍のピーク強度の濃度依存

- 1 µmol/lまでは比較的容易に4,4'-bpyを検出できる.
- レーザのスポットサイズ〜1 μm^2, ナノロッドの厚さ〜10 nm
  - 1 μm^2 × 10 nmの体積に存在する分子数 →1 µmol/lでは10個以下(6個). 単純計算では1分子計測に近い高感度.

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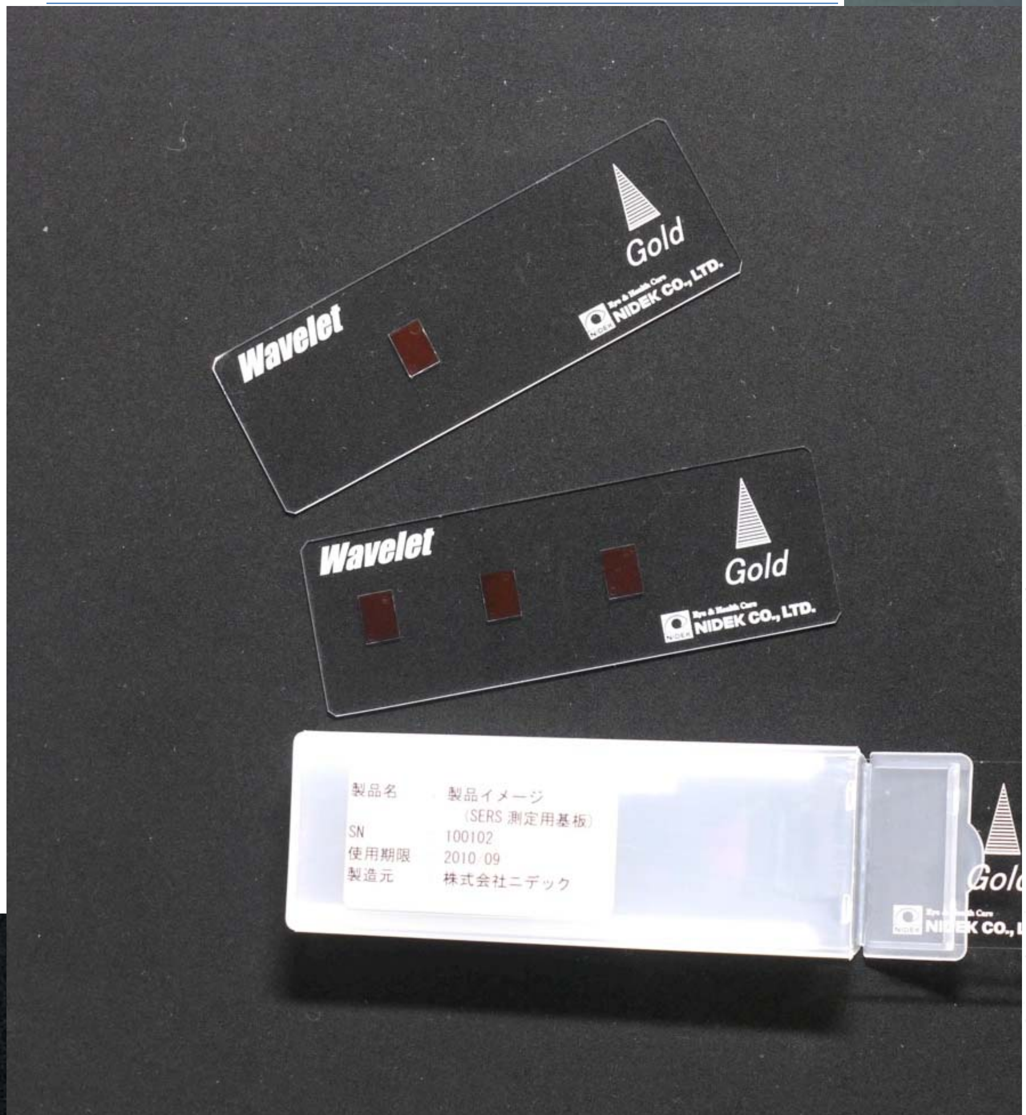

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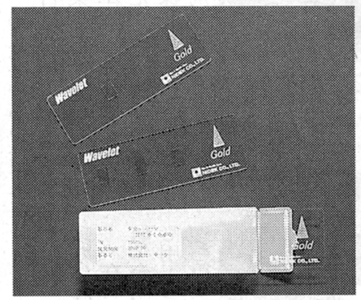
Area News

ニデック（本社蒲郡市拾石町前浜34の14、小澤素生社長、電話0533・67・6611）は、ラマン分光法を用いて物質を分析する特殊基板を開発した。ラマン分光法は物質に単色光を照射し、得られた信号を解析して物質の状態を調べる分析方法の一つ。半導体や医療など先端技術分野で、より詳細な物質分析が可能になる。（蒲郡）

ラマン分光法で詳細に物質分析

ニデックが特殊基板開発



ラマン分光法を用いたＳＥＲＳ測定用Ａｕナノロッドアレイ基板「ウェーブレット」

光を用いた分析法は、大きく分けて赤外分光法とラマン分光法の2種類がある。赤外分光法は主に固体物質を通過した赤外光の量で分析し、ラマン分光法は、物質から跳ね返る光（ラマン散乱光）を信号として検出し、その信号のパターンで物質を分析する。赤外分光法では取り扱いが難しい水溶液などの成分分析も可能になる。

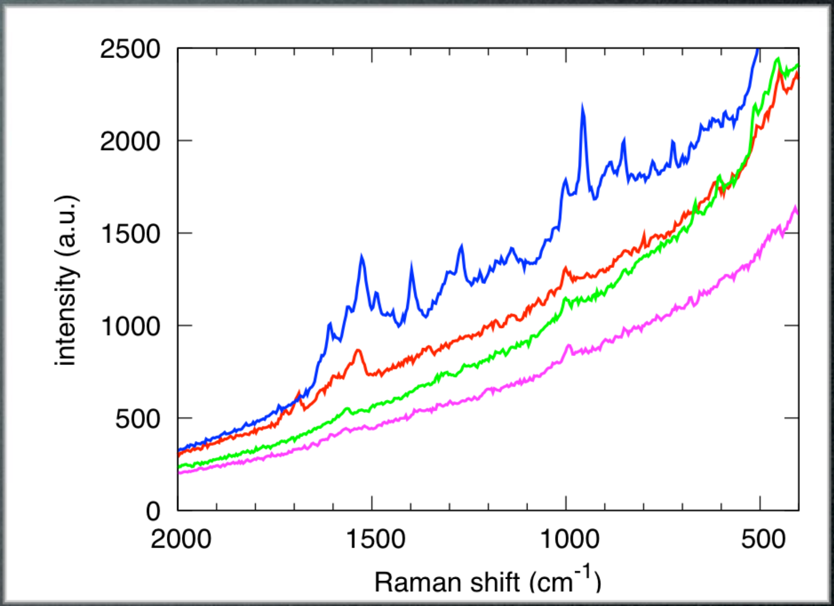
半導体や医薬品など　幅広い分野へ活用

同社が開発したラマン分光法の特殊基板は、長年培った眼鏡レンズや偏光板へのコーティング技術を応用し、真空蒸着でシリカと光を増強させる金をプレートに対して斜めにコーティングする特殊な製法を用いた。物質から跳ね返ってくる光の中から検出したい信号の感度を約1千万倍から1億倍まで引き上げ、より高感度な分析が可能になる。同様の基板を開発・製造する企業は海外に数社あるが、国内メーカーでは初めて。

ラマン分光法を用いた物質分析は、一般的に広く用いられる赤外分光法に比べてまだ普及が限定的なことから、今後は各種研究・分析、半導体、医薬品業界、環境関連など幅広い分野での活用が見込まれる。

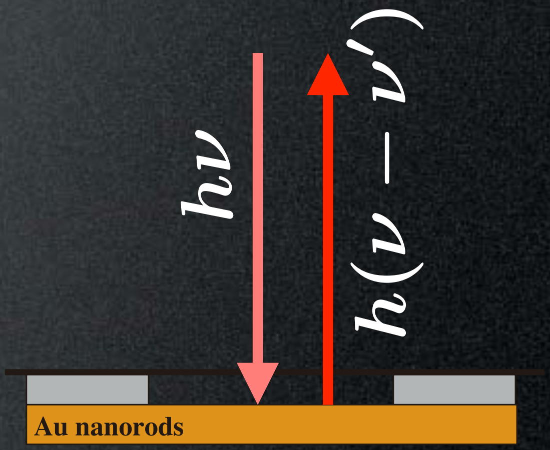
SERS spectra on Au nanorod arrays

- SERS in the water solution is rather stable and reproducible.
- Unidentified peaks appear when SERS is measured without analyte.
- Spectra are spatially & temporary unstable.



SERS spectra of air

Unidentified peaks are due to the contaminations on the surface of Au nanorods. Contaminations may cause serious problems for the highly sensitive Au nanorod arrays.



Self-cleaning SERS Sensors
(日本板硝子材料工学助成会 助成研究)

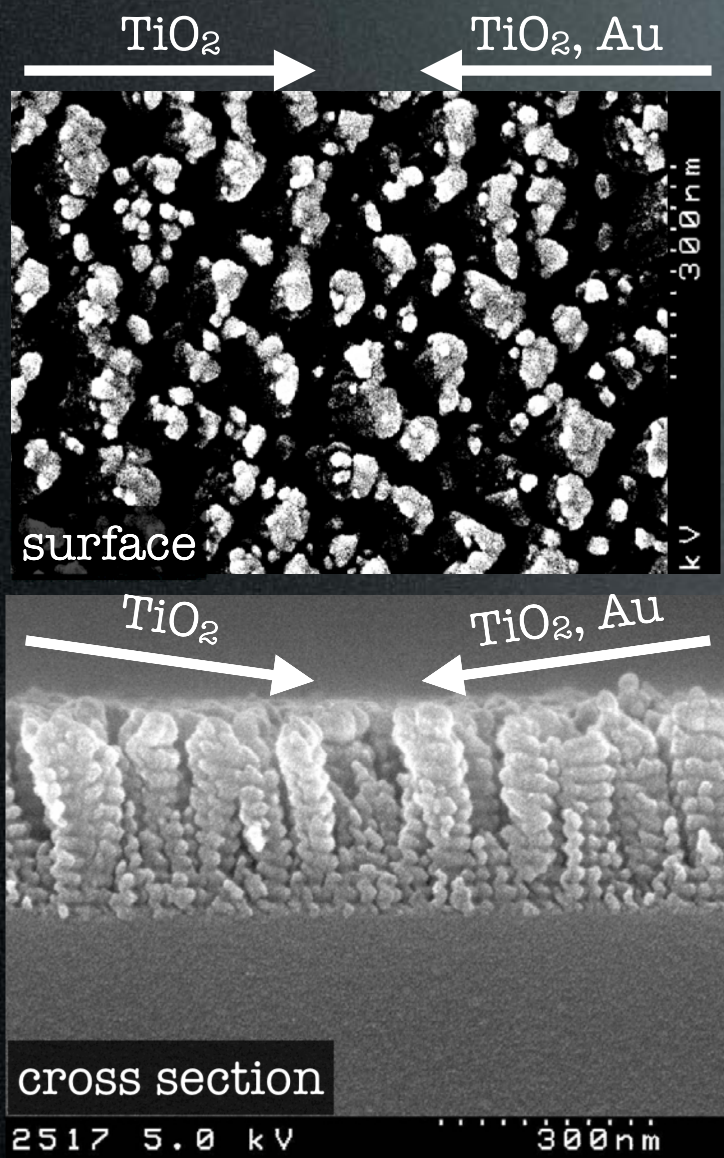
Cleaning contaminations

plasma treatment [1]	☺	Vacuum equipment is required beside Raman Microscope
UV-O_3 treatment	☹	Less effective (preliminary experiment)
self-cleaning by PC	?	• No expensive equipment • Quick **in situ** cleaning • Additional effects

[1] R. J. Walsh and G. Chumanov, "Silver Coated Porous Alumina as a New Substrate for Surface-Enhanced Raman Scattering," App. Spectroscopy **55** (12), 1695-1700 (2001).

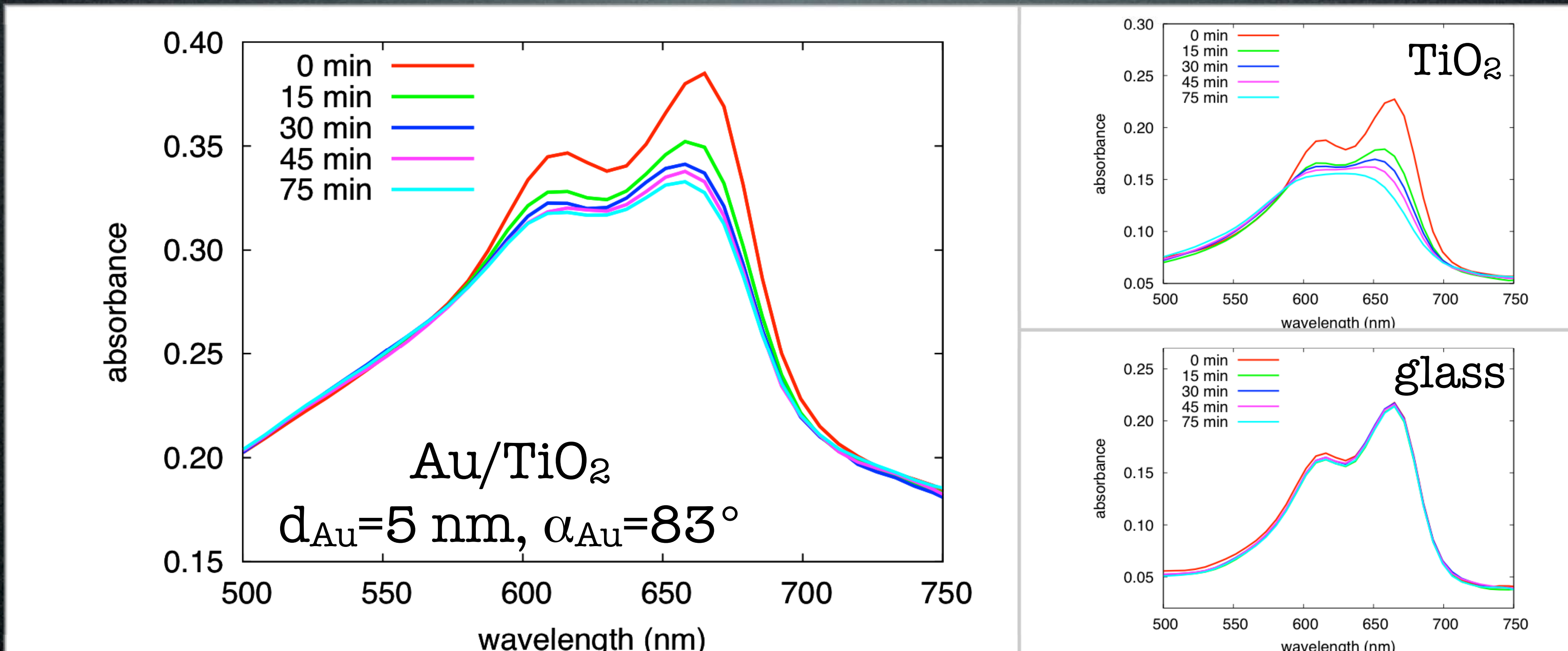
- Feasibility study of self-cleaning SERS sensors; Au/TiO_2

Morphology

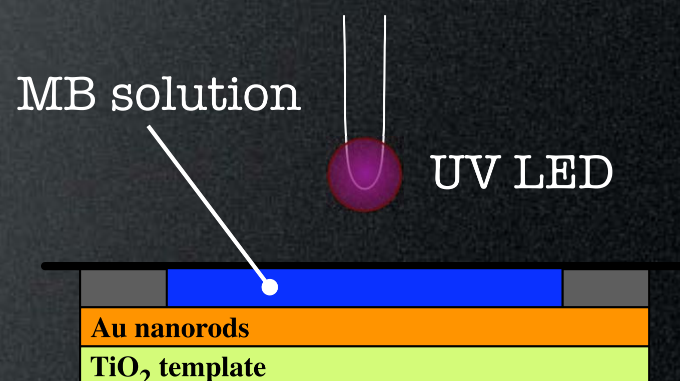


- Anisotropic columnar TiO_2 template was successfully grown.
- Elongated Au nanoparticles were grown on the template.
  - Average length: 93 nm
  - Average width: 43 nm
  - Average aspect ratio: 2.1

Photocatalysis of Au/TiO_2 nanorod arrays

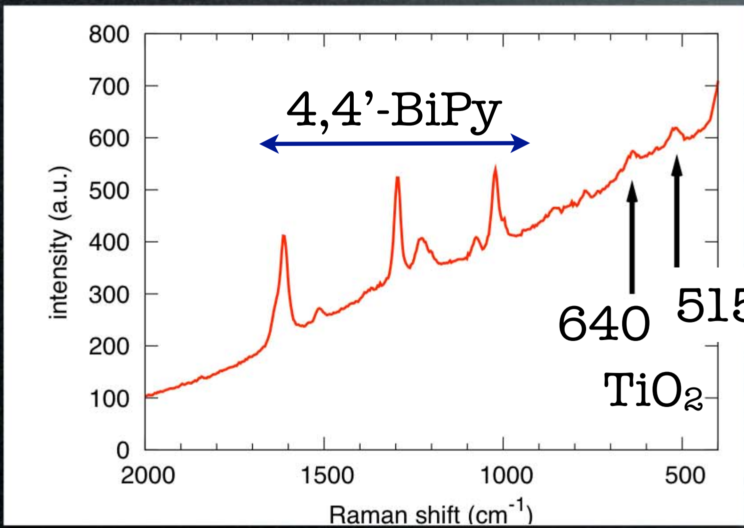


- TiO_2 template works as a photocatalyst even for the sample with Au nanorods.

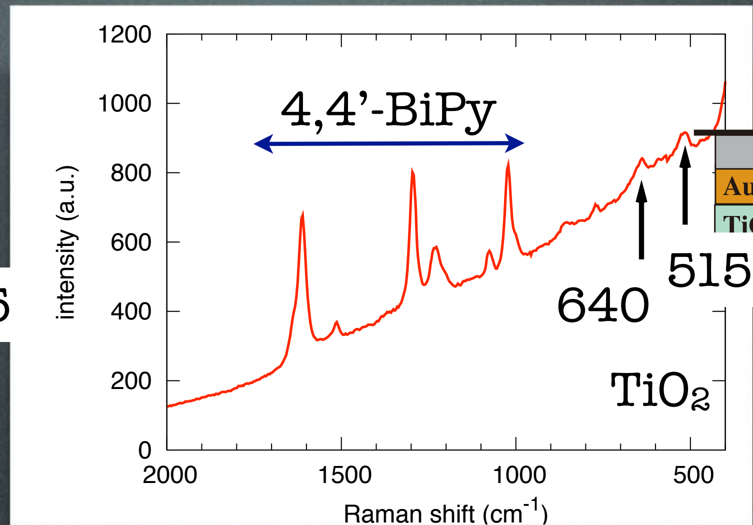


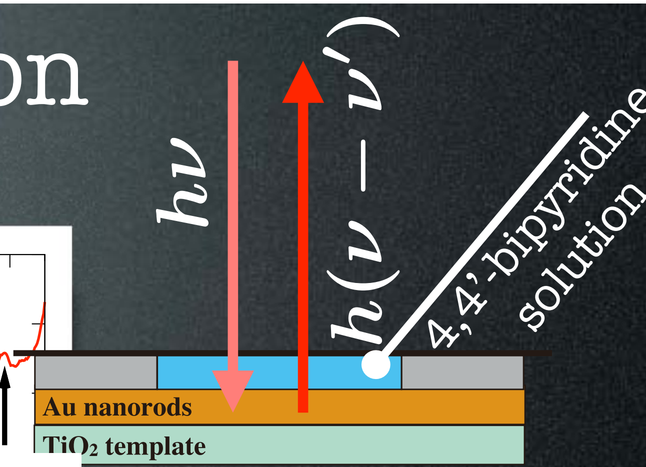
SERS of 4,4'-bipyridine solution

d_{Au}=5 nm, α_{Au}=83°



d_{Au}=10 nm, α_{Au}=73°

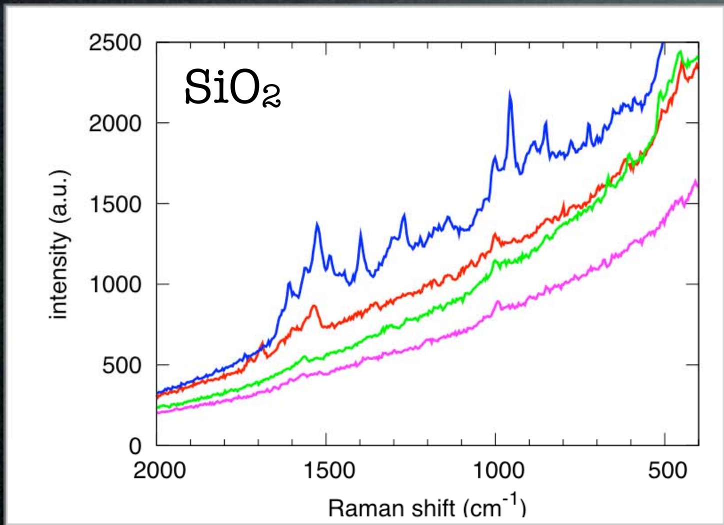


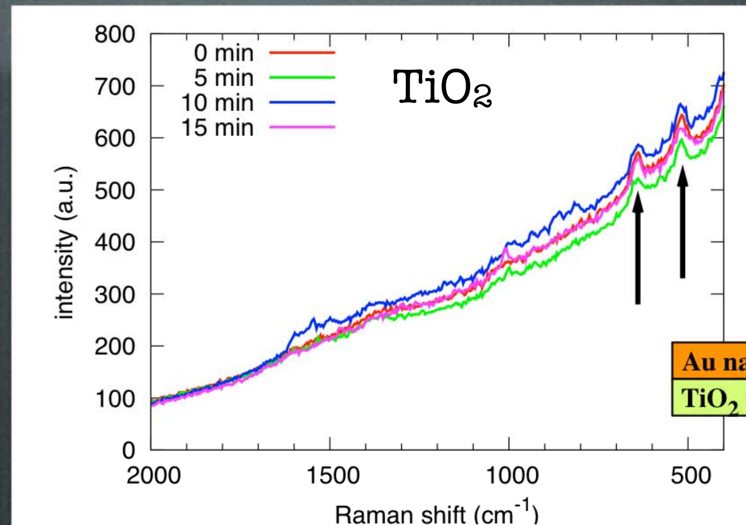


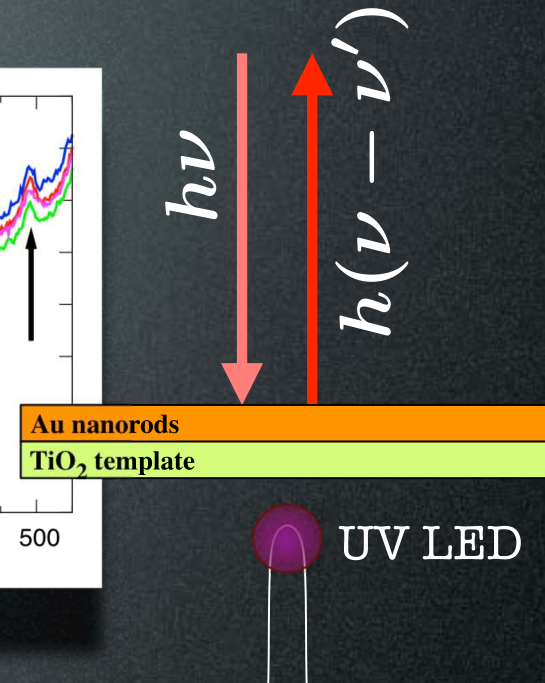
- Well enhanced Raman spectra of 4,4'-bipyridine are obtained.
- Peaks at 515 cm^{-1} & 640 cm^{-1} are identified as TiO_2 anatase. [1]
  - TiO_2 is in contact with Au nanorods.
    ☛ The surface of the Au nanorods is expected to be cleaned by the chemically active species generated at the photocatalytic TiO_2 surface.

[1] P. J. Huang, H. Chang, C. T. Yeh, and C. W. Tsai, "Phase transformation of TiO2 monitored by Thermo-Raman spectroscopy with TGA/DTA," Thermochimica Acta **297** (1-2), 85-92 (1997).

SERS of air with UV irradiation

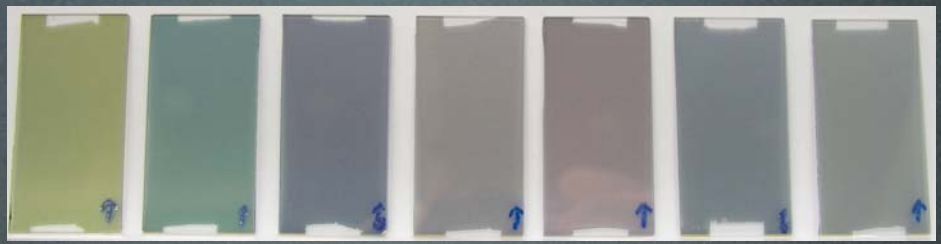






- No significant unidentified peak is observed.
- SERS spectra are stable spatially & temporally.
  - Such stability has never been achieved for NRA on SiO_2.

- Self-cleaning effect of template stabilizes the SERS properties of Au nanorod arrays.



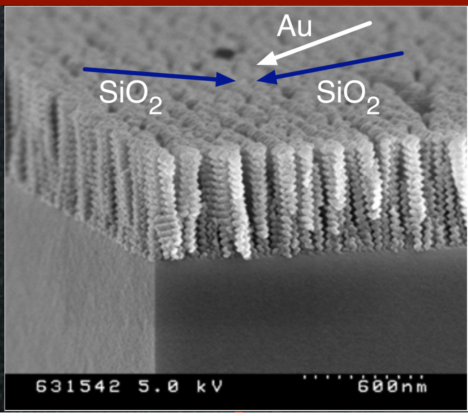
t_{SiO_2} [nm]	0	0	100	300	300	300	500
α_{Au} [°]	0	73	73	73	0	85	73

- ~50% of incident light is reflected or transmitted to far field. Further enhancement of SERS is expected by improvement of coupling of local plasmon with photon.

Further enhancement of SERS by Local Plasmon Resonator

Progress of our research on nanoparticles

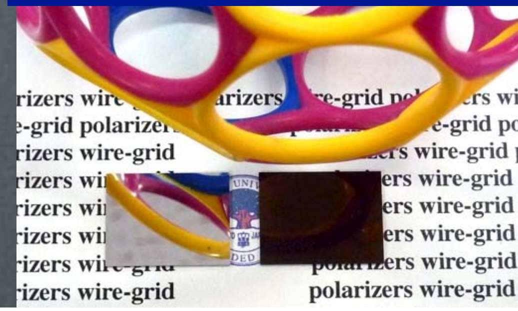
Au, Ag nanorod arrays



M. Suzuki *et al.*, "Direct formation of arrays of prolate Ag nanoparticles by dynamic oblique deposition," Jpn. J. Appl. Phys. Part 2 **44** (1-7), L193-L195 (2005).

Polarizer

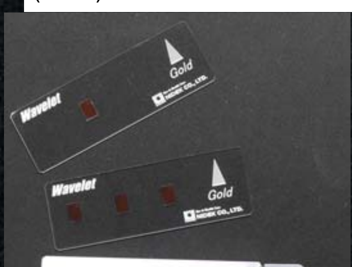
LR-WG polarizers



M. Suzuki *et al.*, "Low-reflective wire-grid polarizers with absorptive interference overlayers," Nanotechnology **21** (17), 175604 (2010).

SERS & PC-SERS

M. Suzuki *et al.*, "In-line aligned and bottom-up Ag nanorods for surface-enhanced Raman spectroscopy," Appl. Phys. Lett. **88** (20), 203121 (2006).



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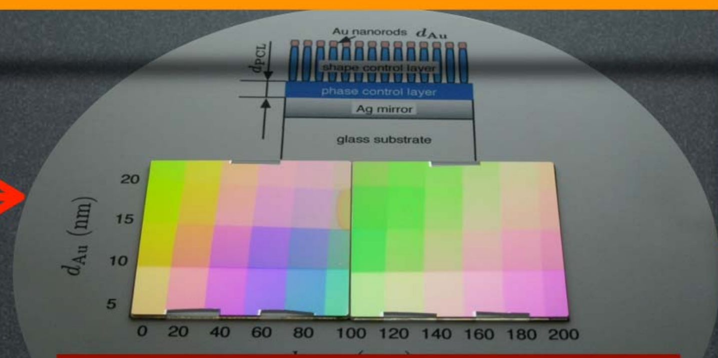

Local plasmon resonator for SERS

M. Suzuki *et al.*, "Tailoring coupling of light to local plasmons by using Ag nanorods/structured dielectric/mirror sandwiches," Journal of Nanophotonics **3** (1), 031502 (2009).

- Photothermal devices for micro-fluid?
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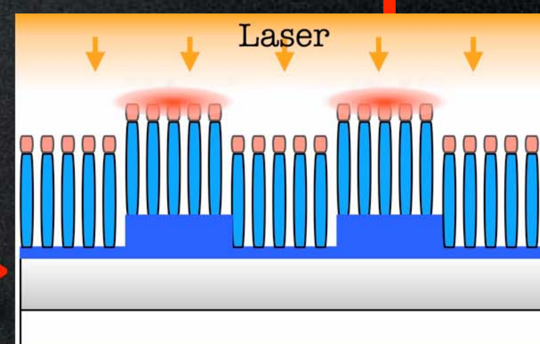
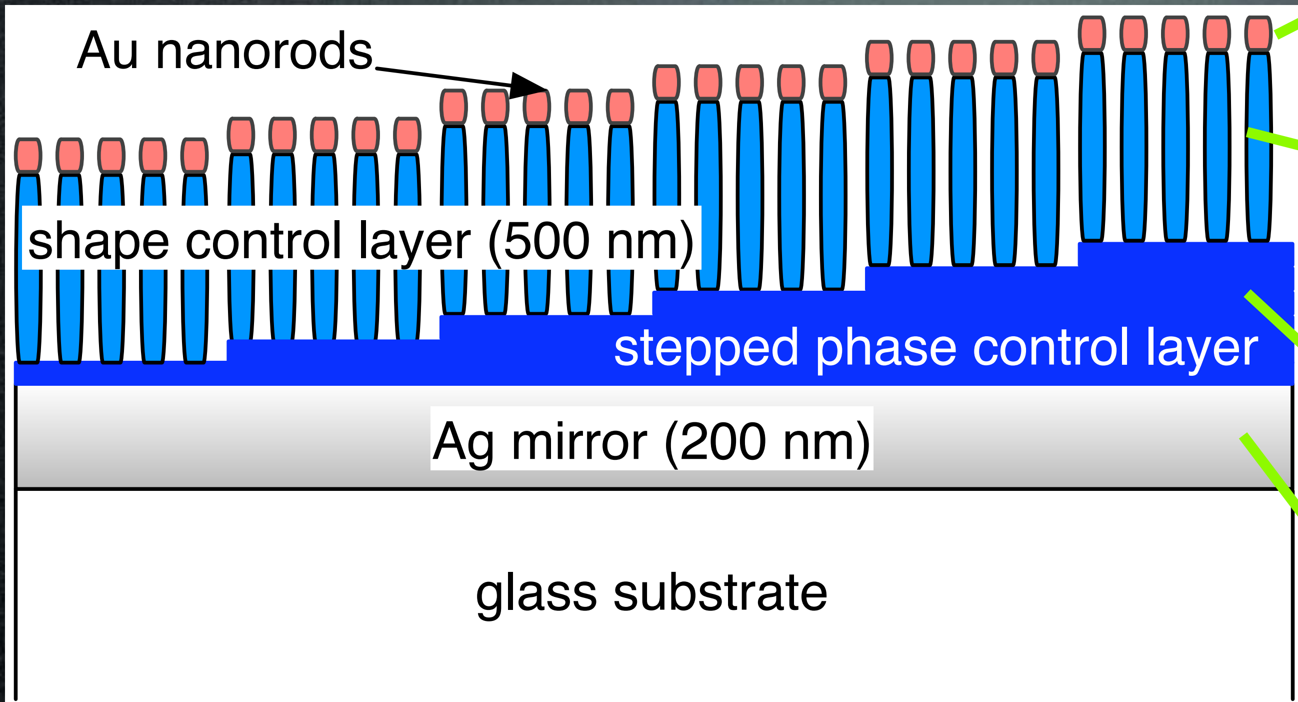


Spatiotemporal nanoheaters

- Nanoparticle absorber
  - Enhanced properties
  - New functions

Preparation of local plasmon resonator (Au NRA/SCL/PCL/Ag mirror)



Au deposited at α=73°, average thickness=10 nm.

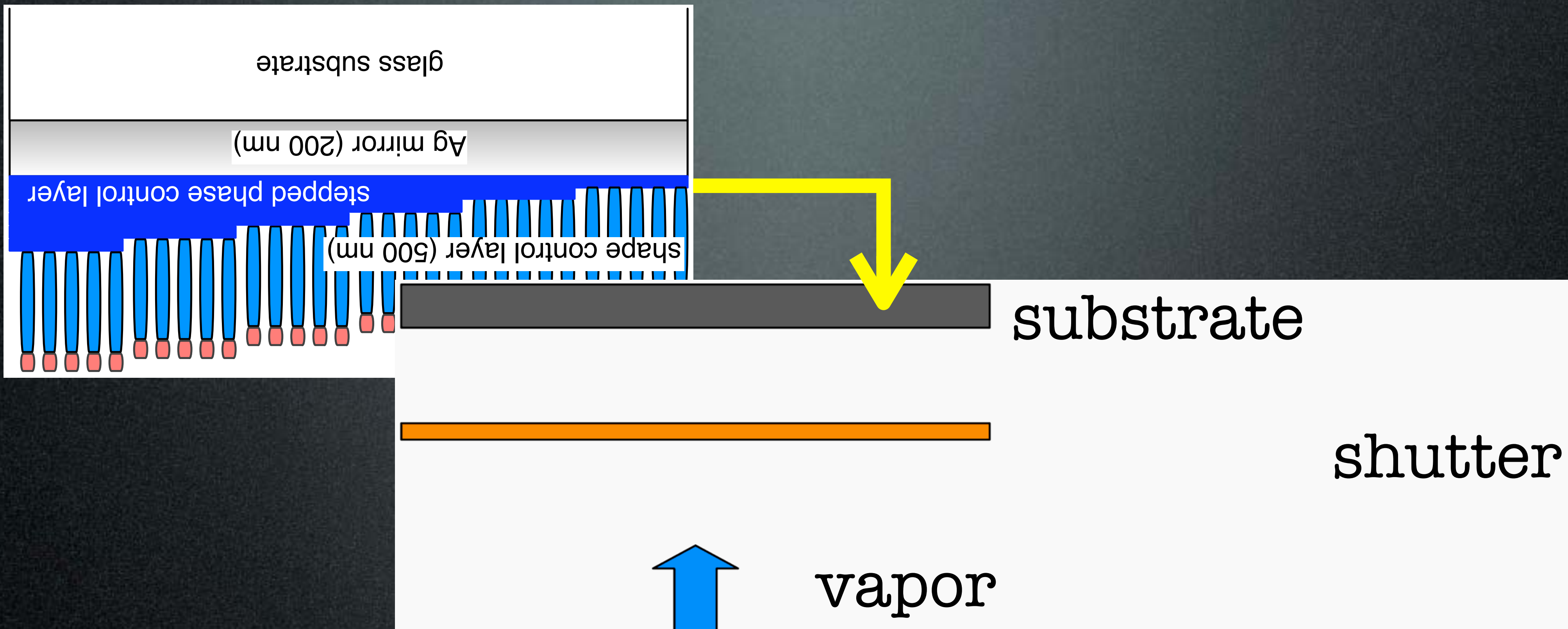
SiO_2 film serial-bideposited at α=79°.

SiO_2 film deposited at α=0°: flat but stepped by moving a shutter. 0 – 200 nm.

Flat Ag film deposited at α=0°

- By recycling the light scattered by nanorods, we tried to enhance the coupling of light to the local plasmon. ≈ To minimize reflectance of Au NRA/SCL/PCL/Ag mirror.
  - Mirror: reflecting the light transmitted through the nanorods.
  - Phase control layer: tuning the optical path length.
- To find the optimum structures quickly, a series of different SiO_2 thicknesses were realized.

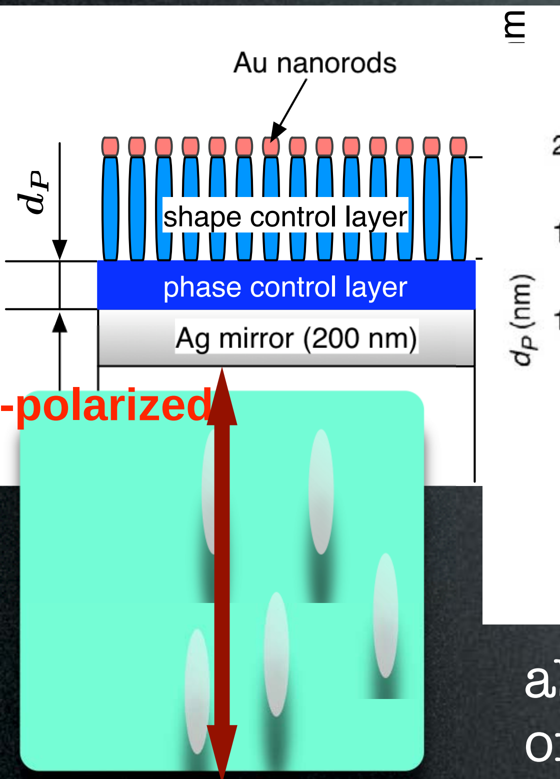
Preparation of stepped phase control layer

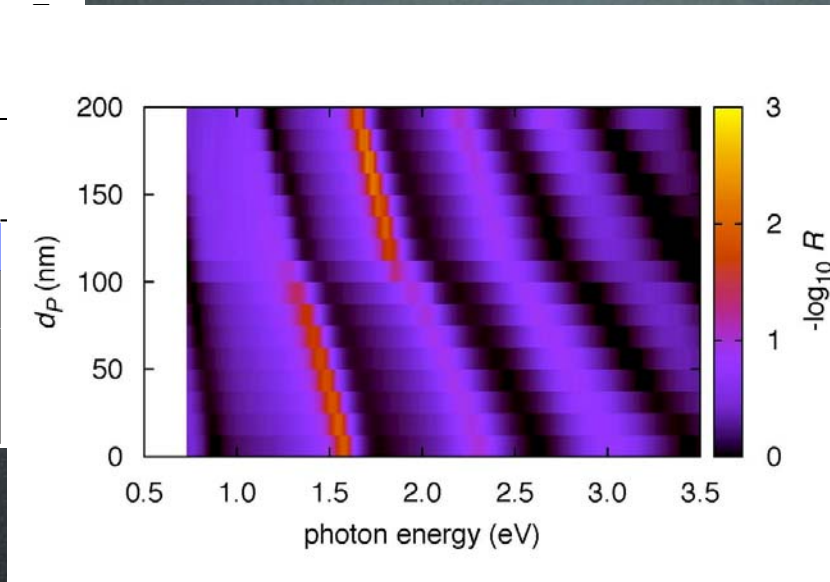


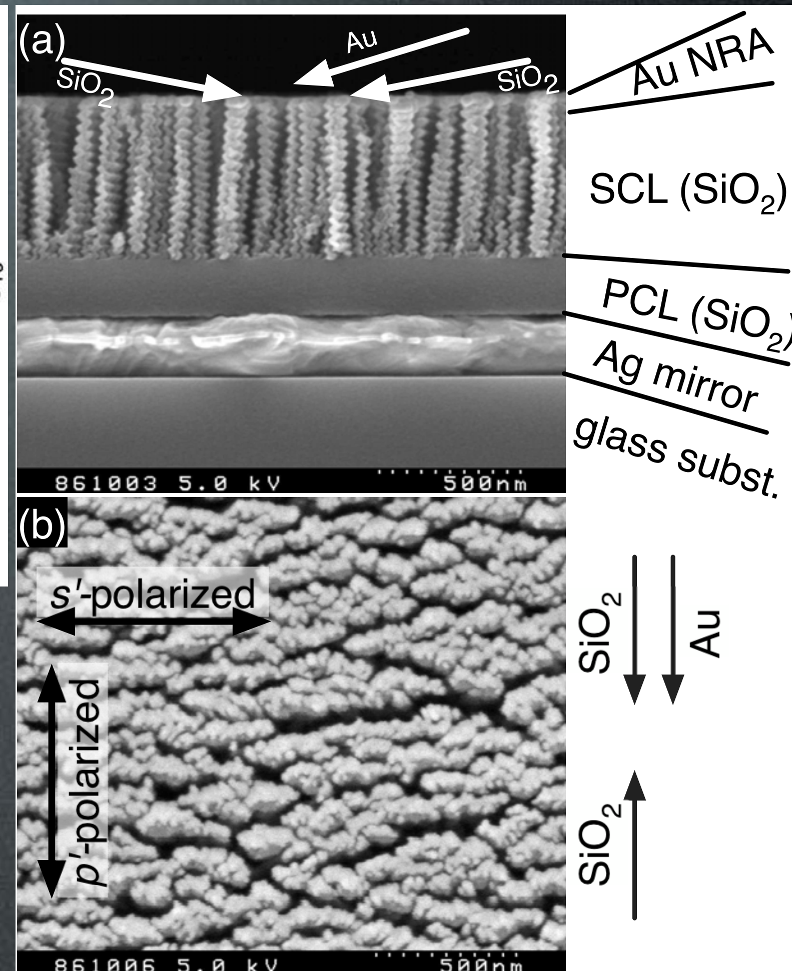
- A series of different thicknesses were realized on a single substrate by moving a shutter incrementally across the sample during deposition.

Morphology & spectra of local plasmon resonators

$d_{\mathrm{Au}} = 10$ nm







abscissa: photon energy
ordinate: thickness of PCL

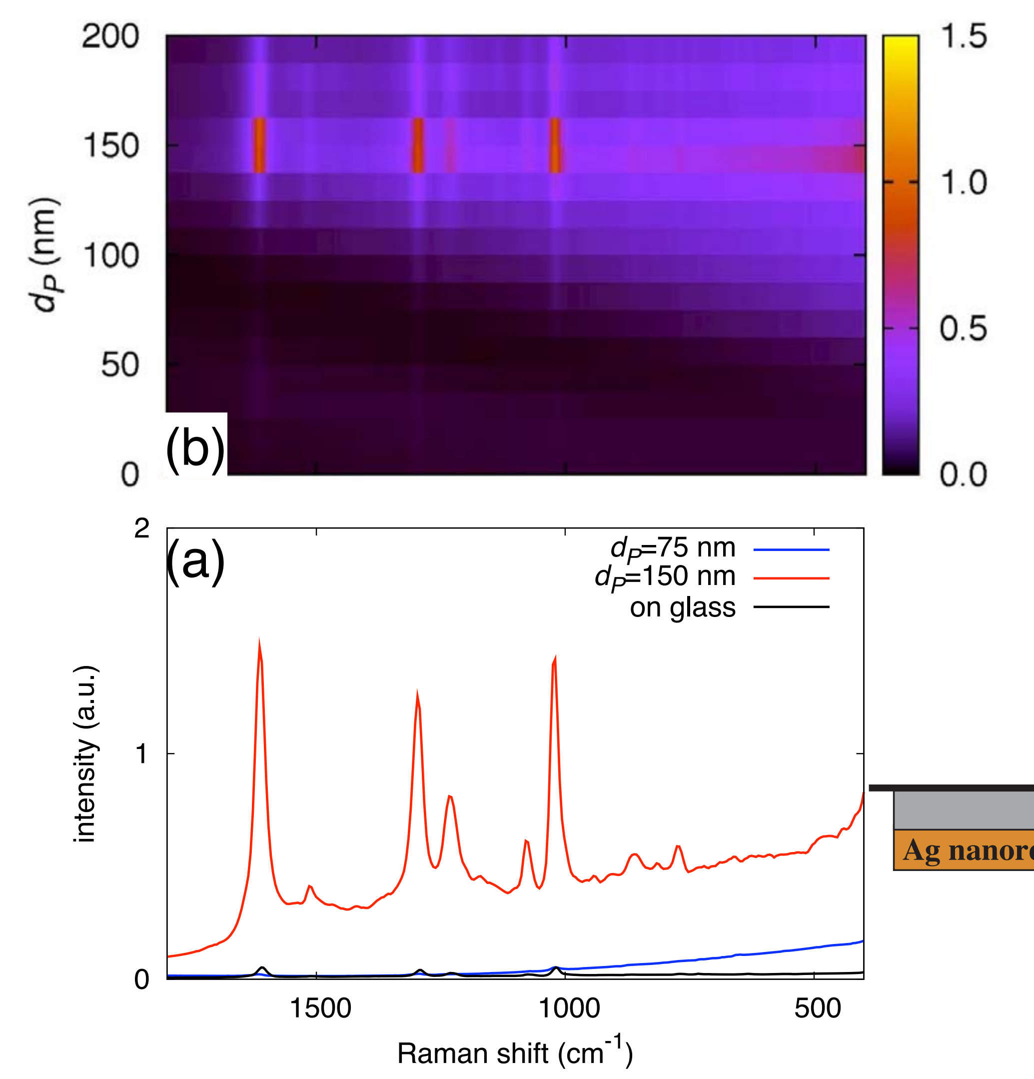
Colors: $-\log_{10} R$

yellow→small R & large absorption

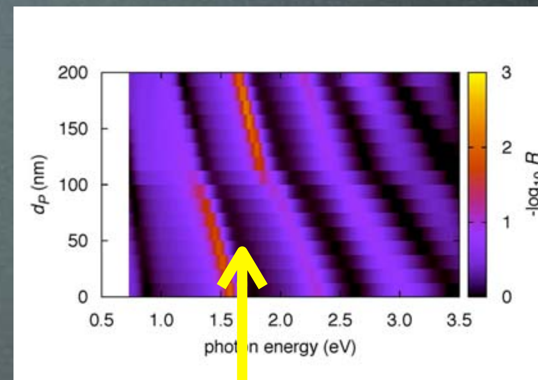
purple →large R & small absorption

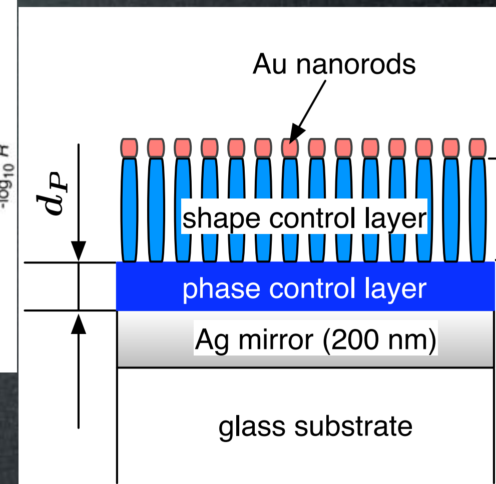
- The designed multilayered structures are successfully realized.
- The reflectance changes periodically as a function of the photon energy.
  - Dark lines: Narrow band perfect reflector
  - Yellow & Red parts: Narrow band perfect absorber
    - Perfect reflector/absorber conditions are tuned precisely by changing thickness of the phase control layer.

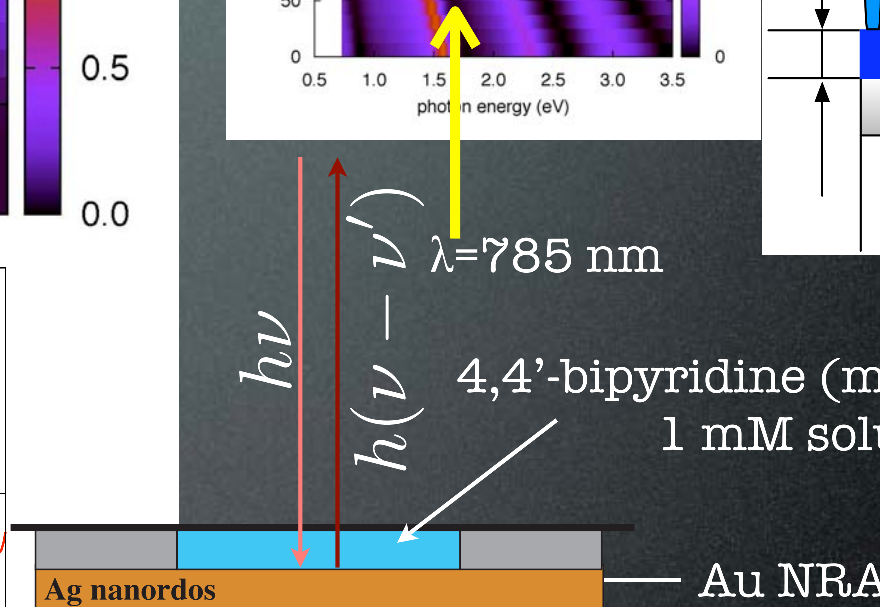
SERS on Au-NRA/SCL/PCL/Ag mirror



Selected SERS spectra and the SERS spectra as a function of d_P.







- SERS is enhanced significantly near AR condition.
  - about **50 times larger** than Au NRA **without mirror**.
- > 10^8 times enhancement is expected.

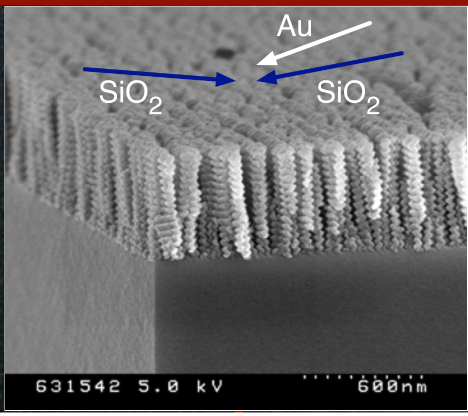
Local Plasmon resonators are efficient to enhance the local electric field.

- Applications: SERS, SEIRA, surface enhanced fluorescence spectroscopy etc.

Novel application of local plasmon resonator to plasmonic nanoheaters

Progress of our research on nanoparticles

Au, Ag nanorod arrays



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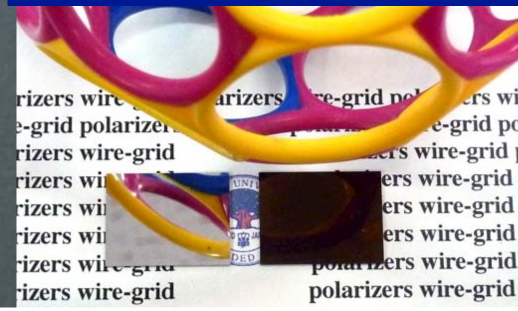
Polarizer

LR-WG polarizers



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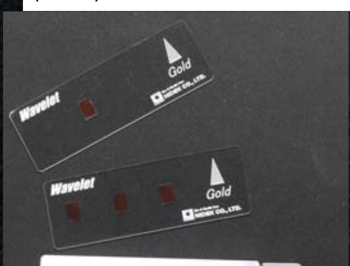

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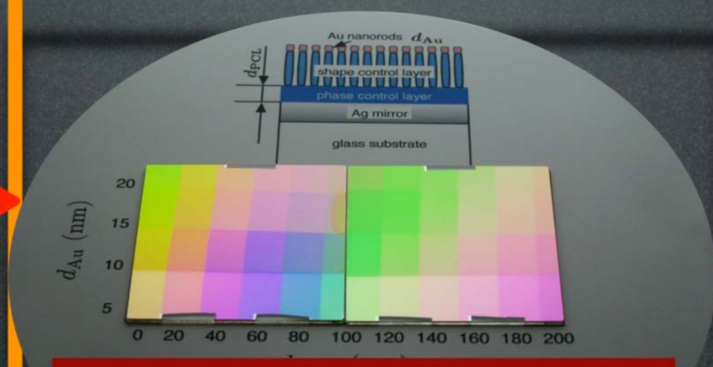

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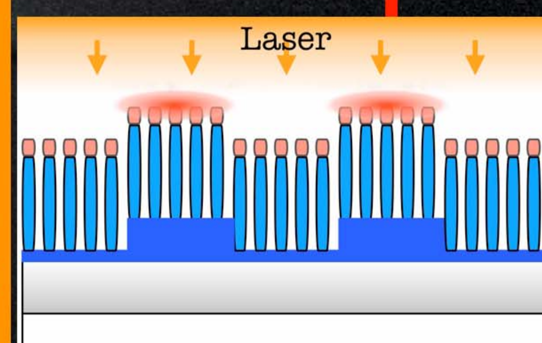
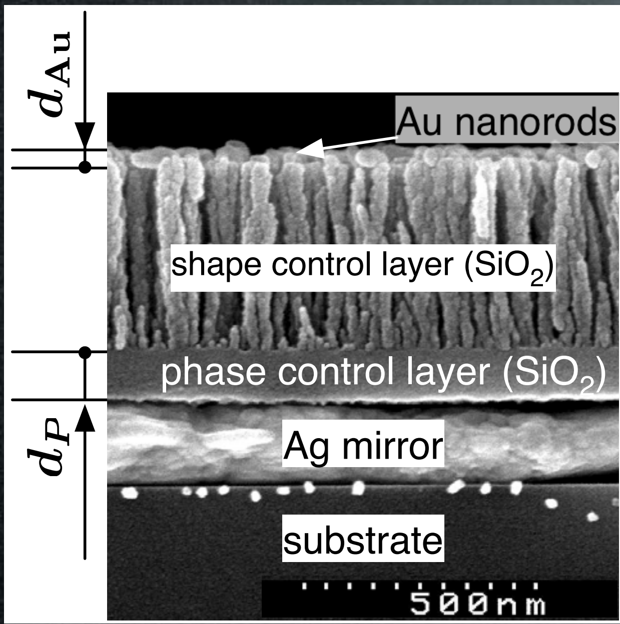
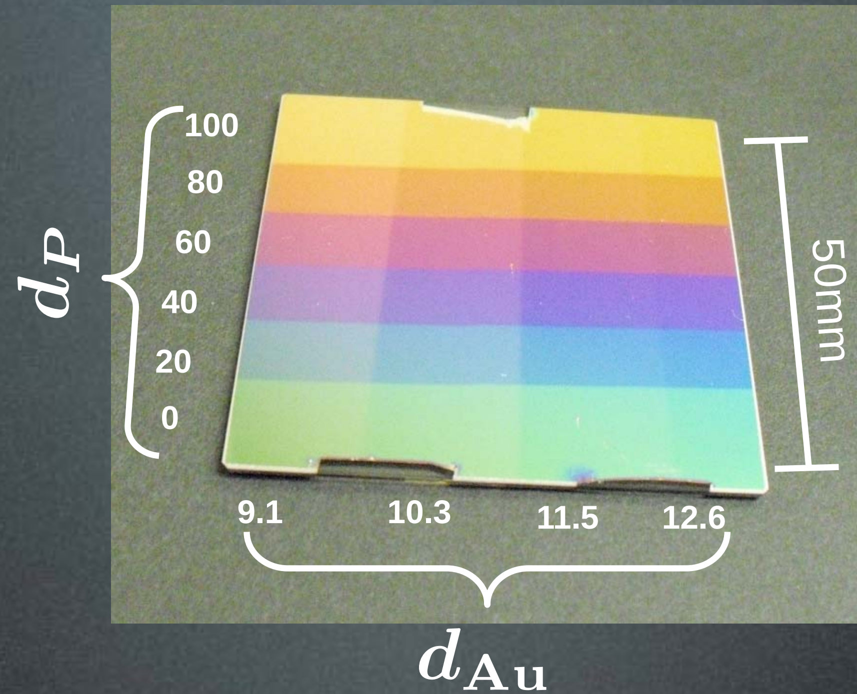


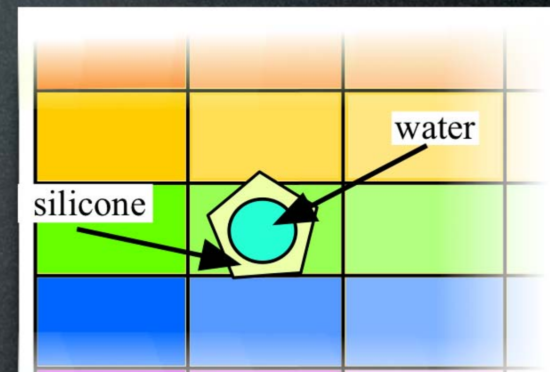
Spatiotemporal nanoheaters

- Nanoparticle absorber
  - Enhanced properties
  - New functions

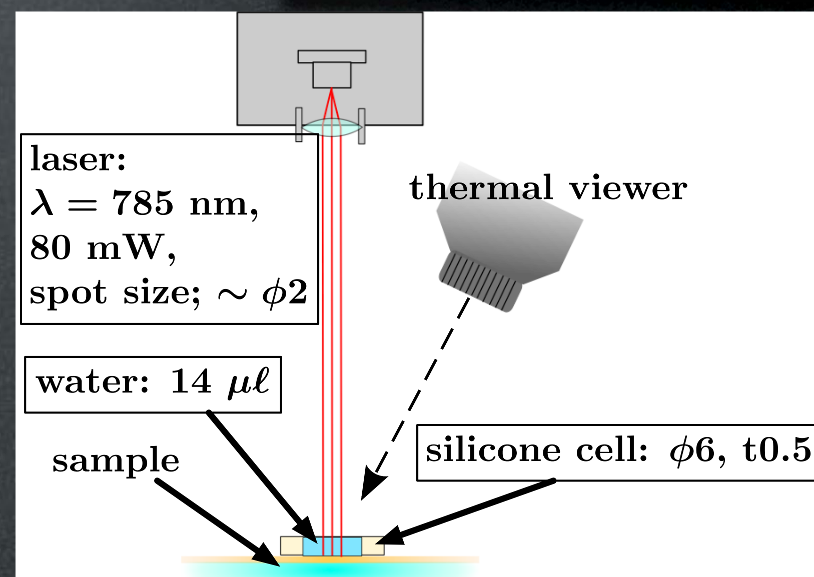
Appearance & morphology of local plasmon resonator chips





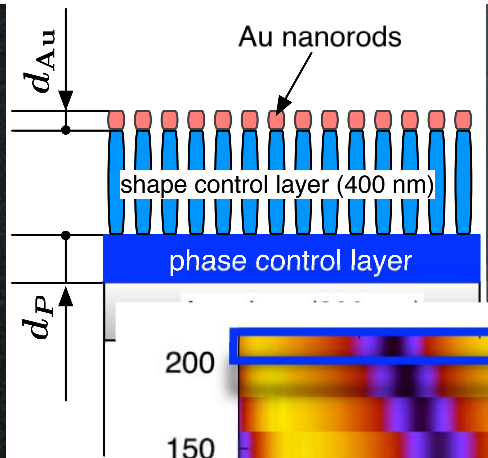


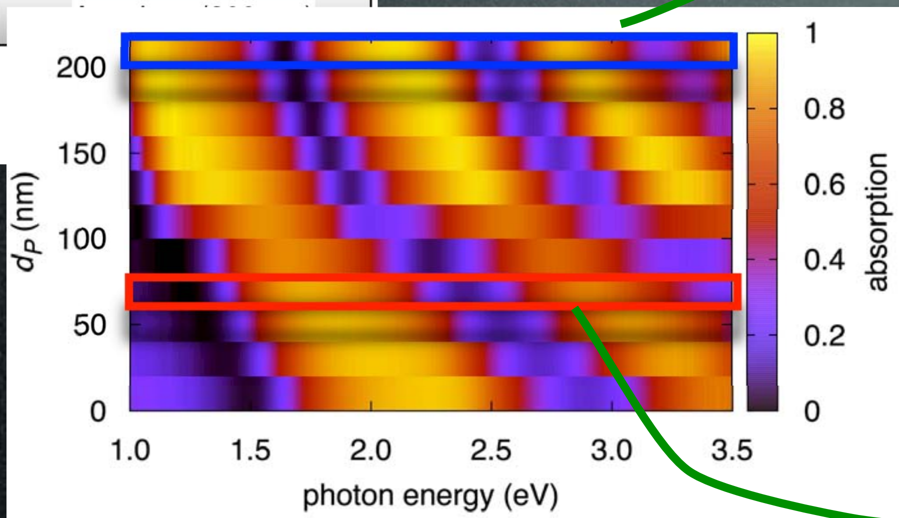
- Multilayered thin films with various combinations of the layer thicknesses have been successfully prepared.
  - The absorption was measured on each chip.
  - The temperature of H_2O in a silicone cell was measured by thermal viewer.

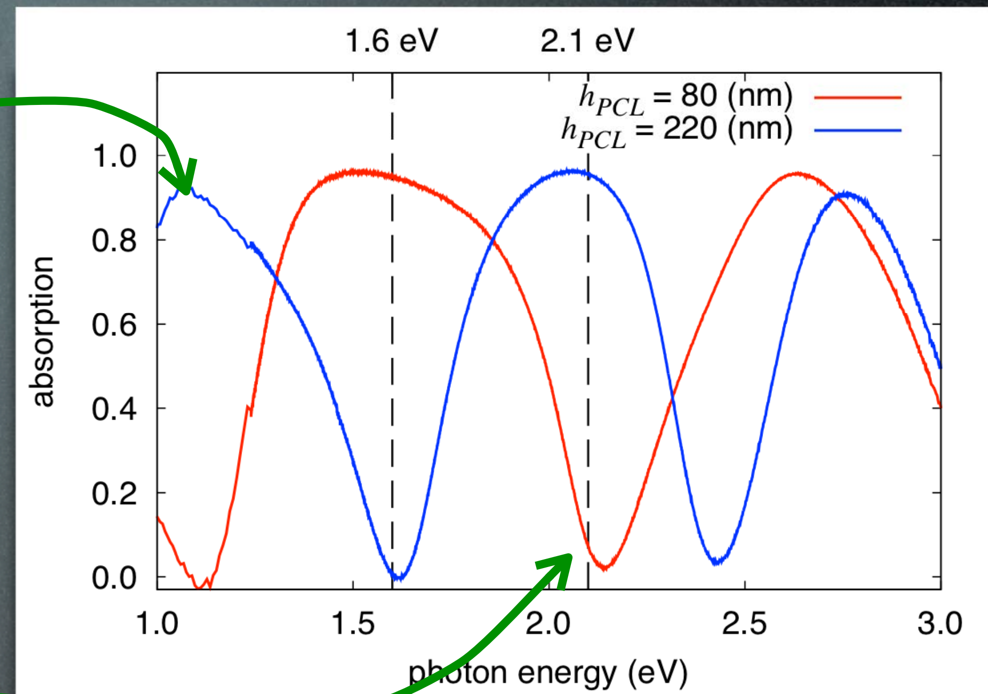


Spatially selective absorption

$d_{\mathrm{Au}} = 9$ nm







- The optical absorption can be controlled between 0~97% by changing d_P.
- When d_P = 80 nm,

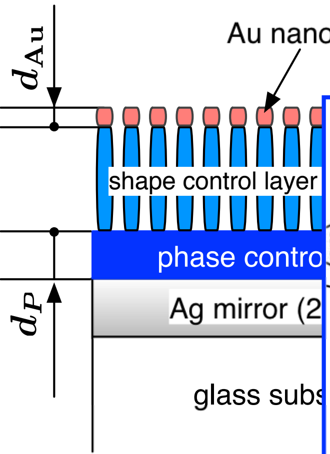
  A ≥ 95% @ 1.6 eV and A ~ 0% @ 2.1 eV.

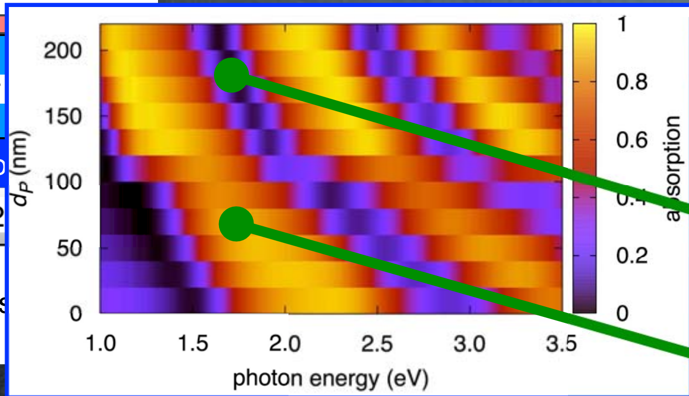
  When d_P = 220 nm,

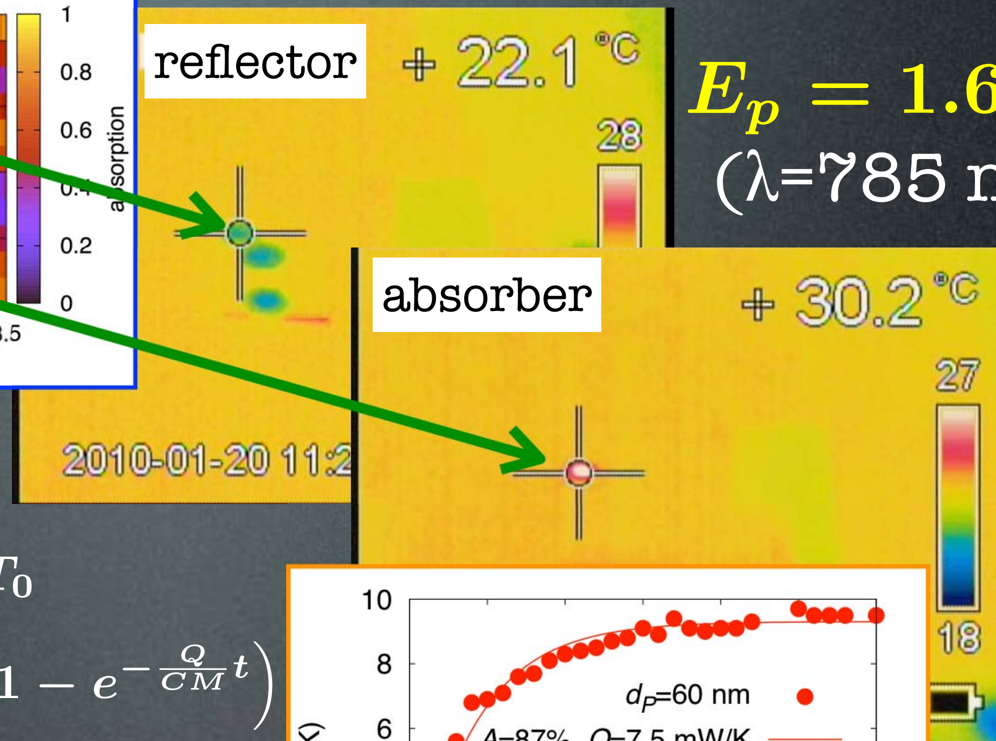
  A ~ 0% @ 1.6 eV and A ≥ 95% @ 2.1 eV.

➡ The high-absorption area can be switched spatially by changing the wavelength of the incident light.

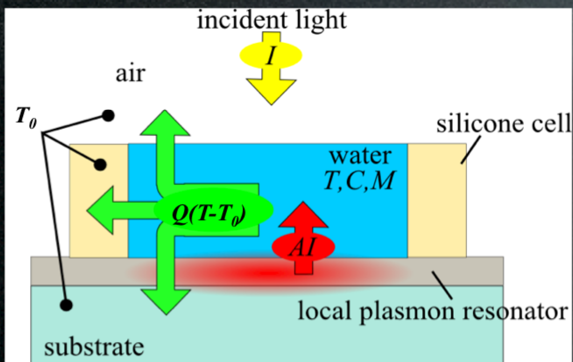
Spatially selective heating $d_{\mathrm{Au}} = 9$ nm





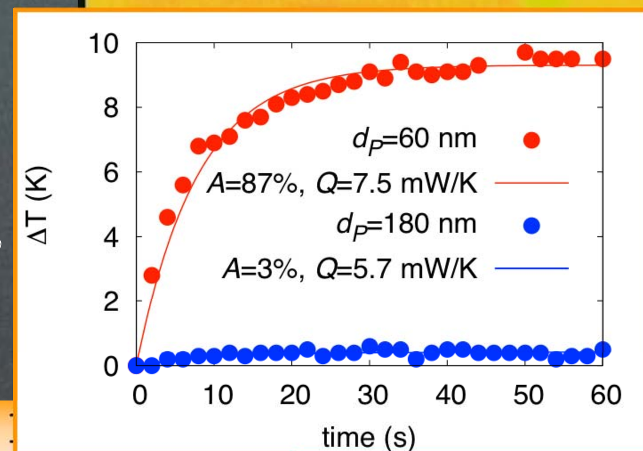


$E_p = 1.6$ eV
(λ=785 nm)

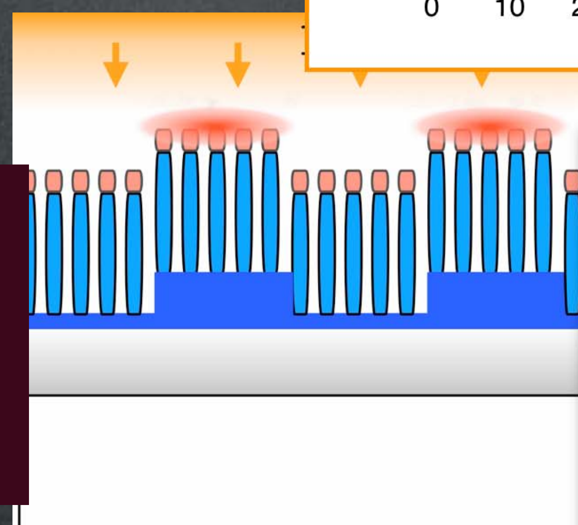


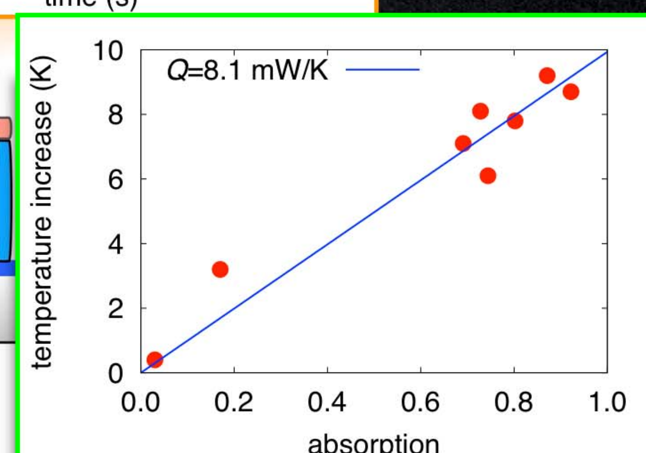
$$\Delta T = T - T_0$$
$$= \frac{AI}{Q}\left(1 - e^{-\frac{Q}{CM}t}\right)$$

Q; heat transfer coefficient, A; absorption, I; laser intensity=80 mW, M; mass of H_2O=14 mg, C; specific heat of H_2O=4.2 J/(g K)



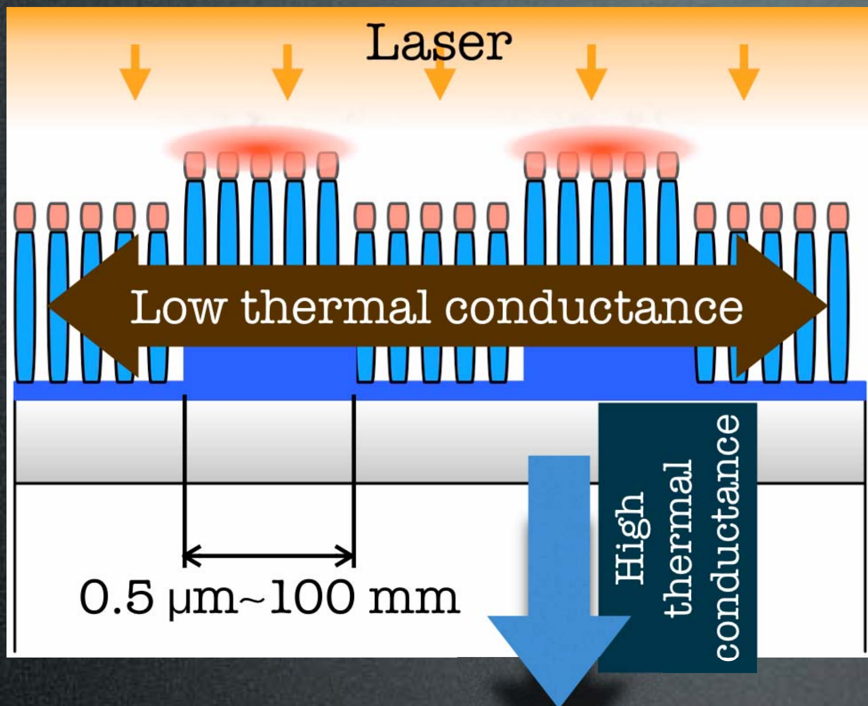
- Temperature variation can be fit with only one parameter of Q.
- $\Delta T_\infty \propto A$

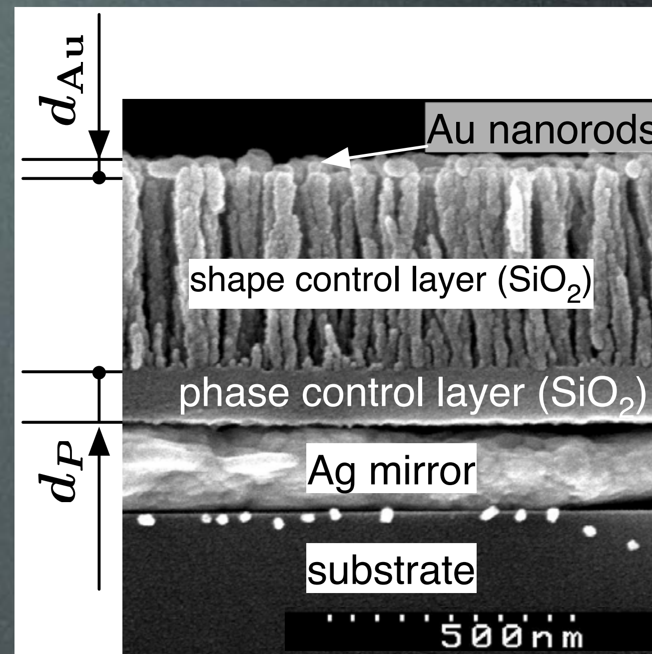




- Photon → Plasmon → Water heating
- The photothermal conversion efficiency is controlled by thickness of PCL.

Proposal: Spatiotemporally controllable nanoheaters



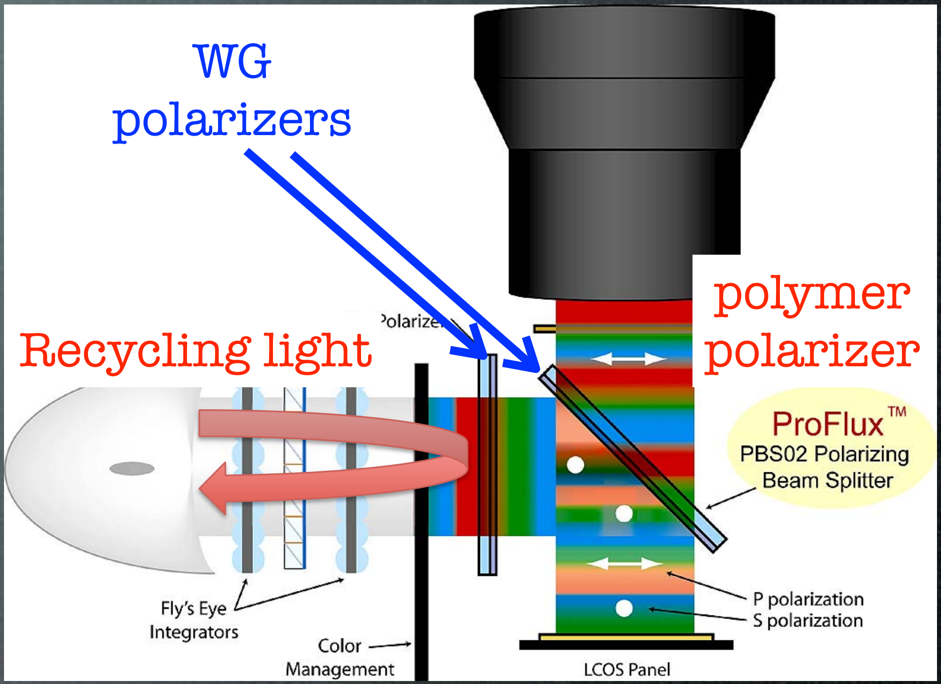


- High photothermal conversion efficiency
  - Perfect absorber/reflector
- High speed
  - Heat is well localized in very small volume
- Multifunction
  - Switching hot area by wavelength/polarization
- Applications
  - Control of micro- and nano-fluid
  - Manipulation of molecules

Low-reflectivity wire-grid polarizers with nanoparticle resonator

Polarizers in LC-projectors

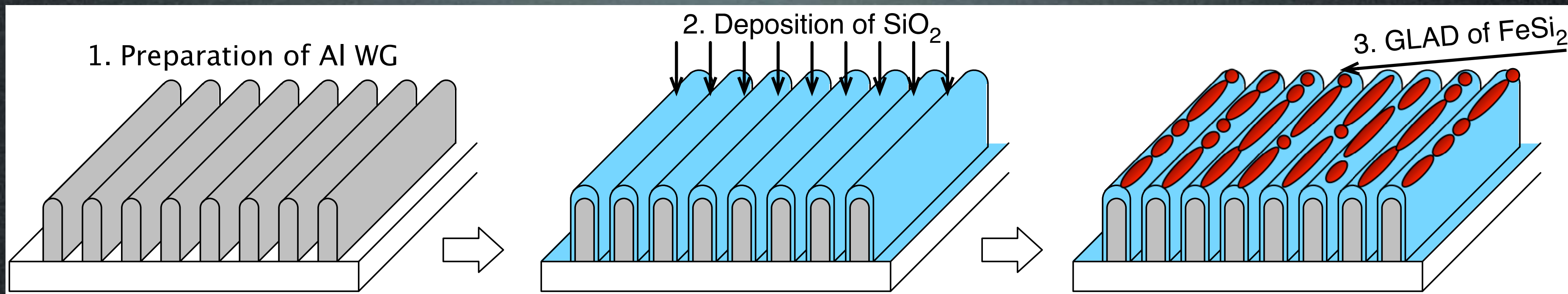
- Al WG-polarizers
  - →High durability; ☺
  - →High R;
  - ☺ Recycling light
  - ☹ Stray light
- Polymer polarizers
  - →Absorptive, low R; ☺
  - →Poor durability ☹



[1] M. Pate, J. Meyer, J. Shiefman, and D. Hansen, "Wire-grid polarizers in modern LCOS light-engine configurations," Journal of the Society for Information Display **14** (3), 275-283 (2006).

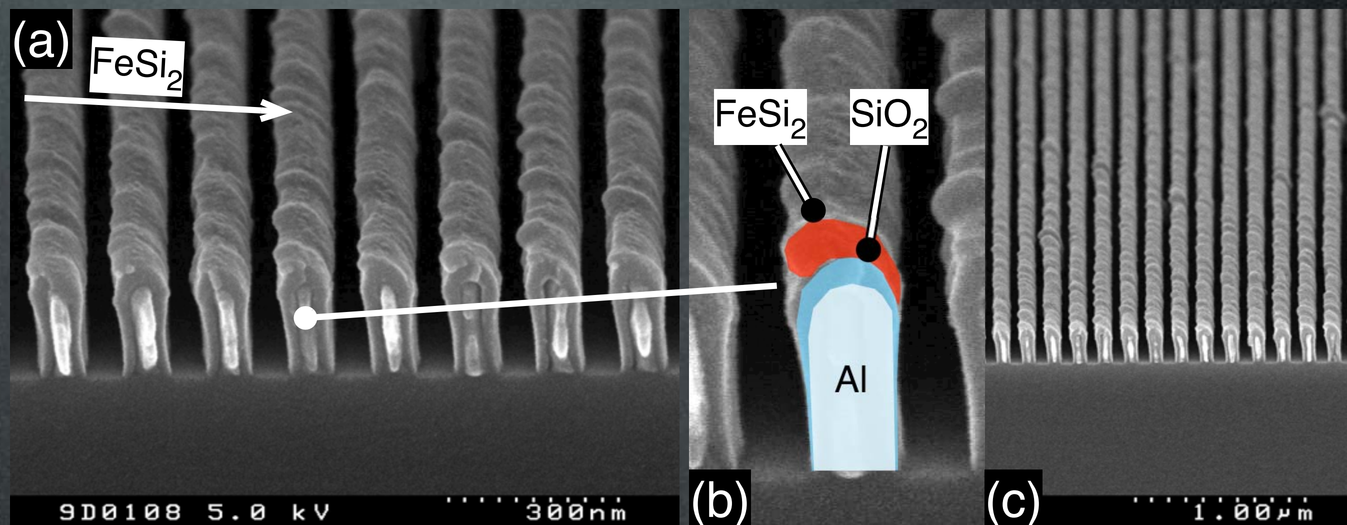
- Development of low-reflectivity (LR) WG polarizers
  - To improve brightness & durability of projectors by replacing polymer polarizers with LR-WG polarizers
  - → AR coatings for metal substrate are required.

Fabrication of LR-WG polarizers



Al WG:
width; 60 nm,
height; 190 nm,
pitch; 150 nm

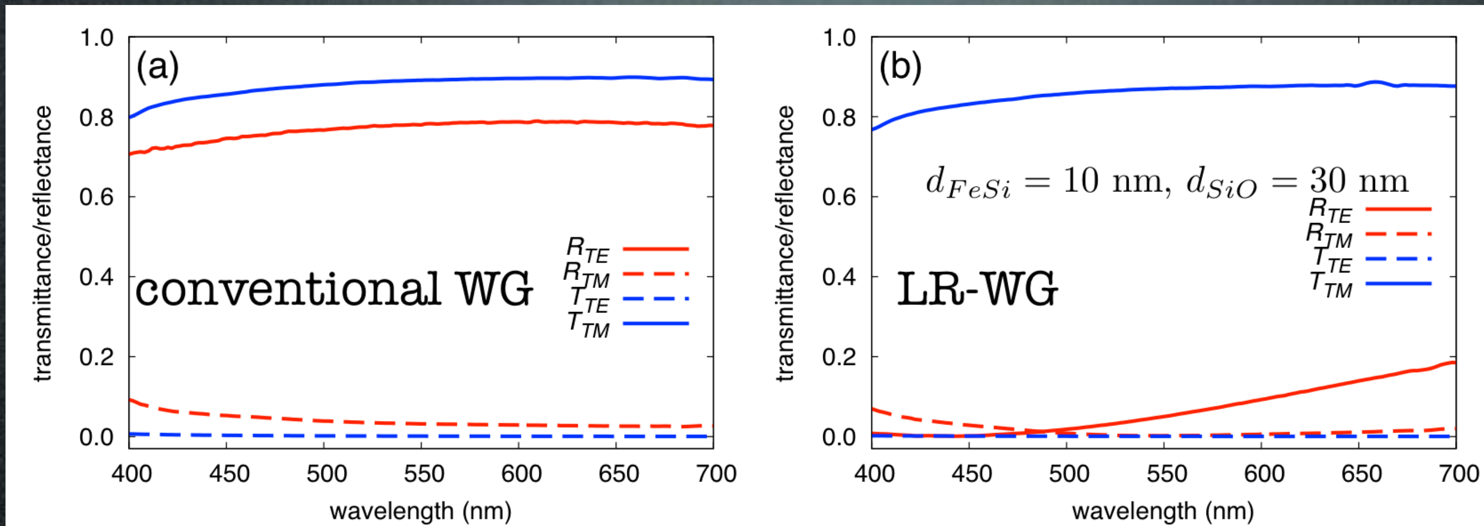
$$d_{FeSi} = 10 \text{ nm}$$
$$d_{abs} \sim 30 \text{ nm}$$
$$d_{SiO} = 24 \text{ nm}$$
$$d_{gap} \sim 24 \text{ nm}$$

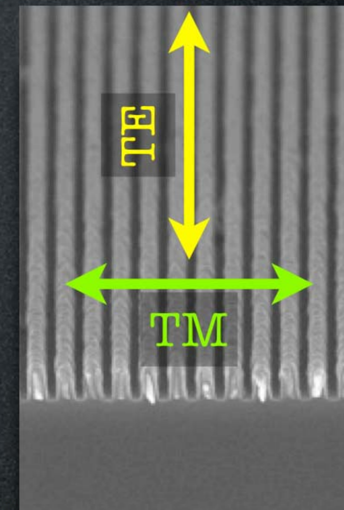


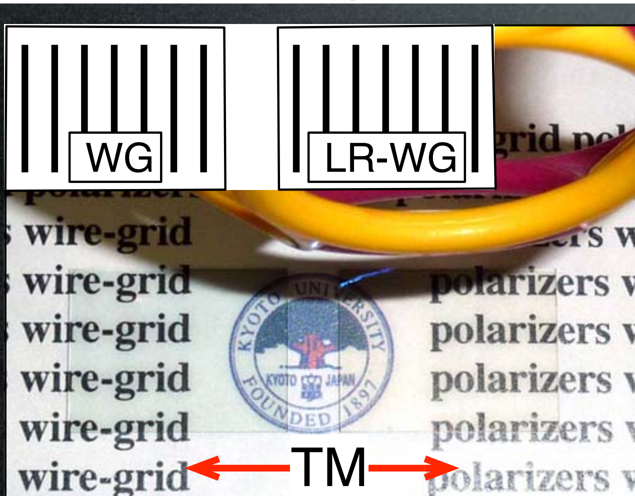
- Fabrication of Al WG polarizers by interference lithography & dry etching. → Normal deposition of gap layer (SiO_2).
- GLAD of absorptive layer($FeSi_2$) at α=87°

➡Elongated $FeSi_2$ nanoparticles are arrayed on the Al WG covered with the gap layer of SiO_2.

Reflection & transmission spectra of LR-WG polarizers



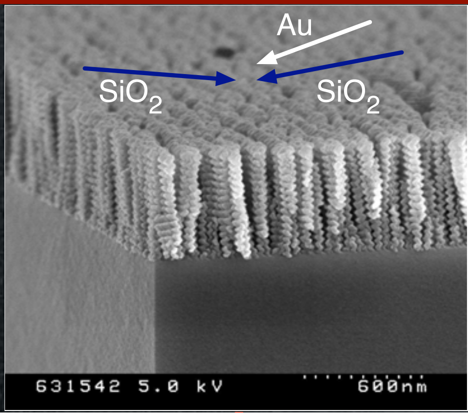




- Spectra
  - The reflectance of LR-WG is very much smaller than that of conventional one,
  - No significant degradation of the transmission properties is recognized
- Visual appearence
  - TM: Both polarizers appear almost completely transparent.
  - TE: LR-WG appears much darker than the conventional WG polarizer.

Summary

Au, Ag nanorod arrays



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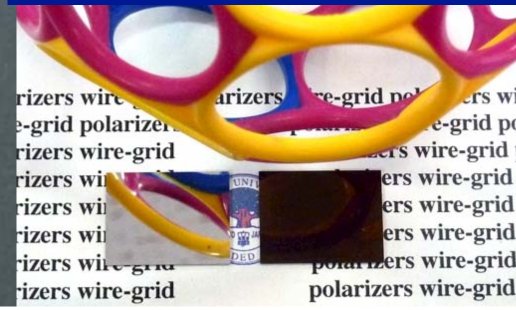
Polarizer

LR-WG polarizers



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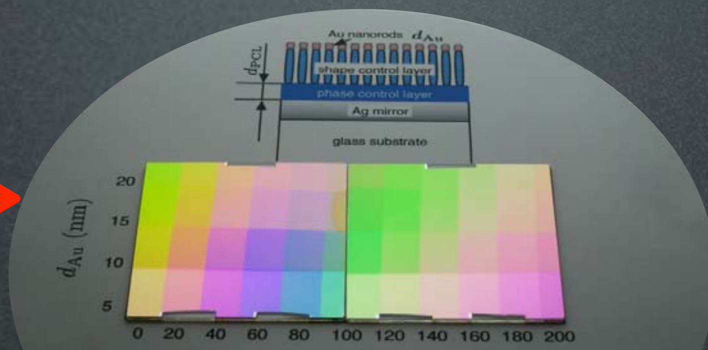

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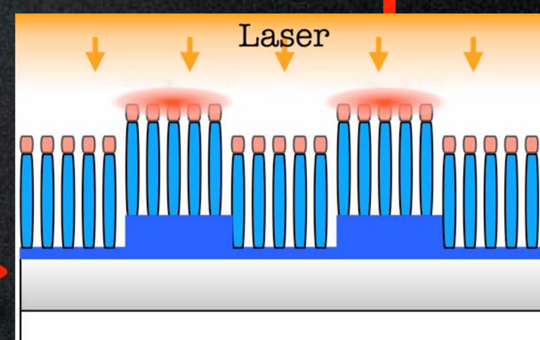

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ACKNOWLEDGMENTS

- Students
  - K. Namura, Y. Imai, R. Tabuchi, H. Tokunaga, S. Li, Y. Wada, W. Maekita
- Coworkers;
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- Collaborators;
  - T. Fukuoka (Univ. Hyogo), Y. Mori (Doshisha Univ.)
  - A. Takada et al. (SONY Info. & Chem. Devices)
  - H. Nakanishi, T. Kawai, S. Oka (NIDEK Corporation)