Three-dimensional metal nano-structures for plasmonic metamaterials

RIKEN Advanced Science Institute Metamaterials Lab.
Hokkaido University Joint Lab.

Takuo Tanaka

14:30-15:00 OECC2010@Sapporo

Outline

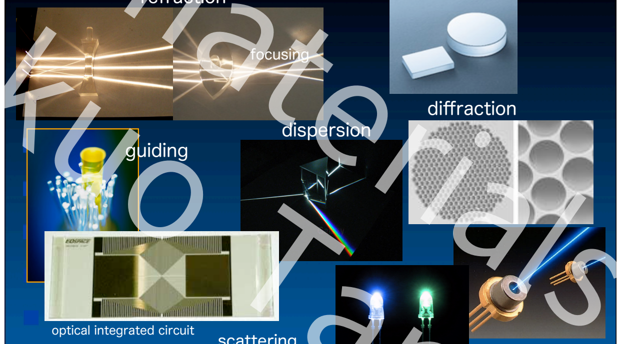
1. Plasmonic Metamaterials - Background
2. Design for plasmonic metamaterials in visible light region
   - What kind of structures are appropriate for metamaterials
3. Laser fabrication technique of 3D metal nano-structures
   - Two-photon-induced metal ion reduction
4. An application of plasmonic metamterial to refractive index control of materials.

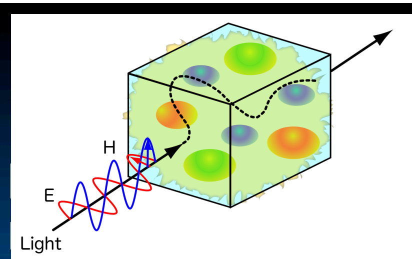
A dream/goal of scientists/engineers in optical and photonics

A dream/goal of scientists/engineers in optical and photonics
is
To manipulate the light with perfect freedom
(control light propagation)

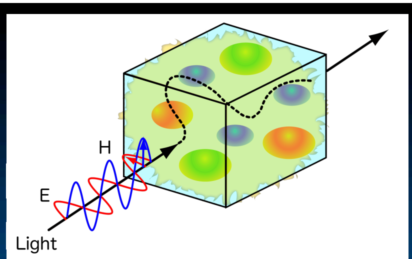
change direction, stopping, transmitting
delivering, modulating, changing color, ...

Manipulate the light (photon)



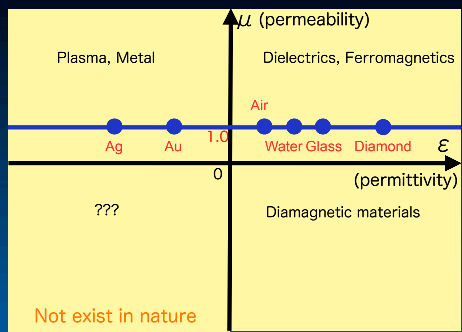


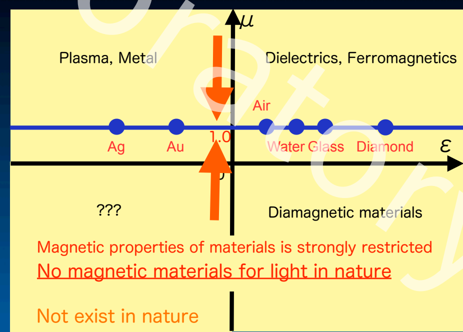
History of optics/photonics is the history of design and fabrication of index distributions.

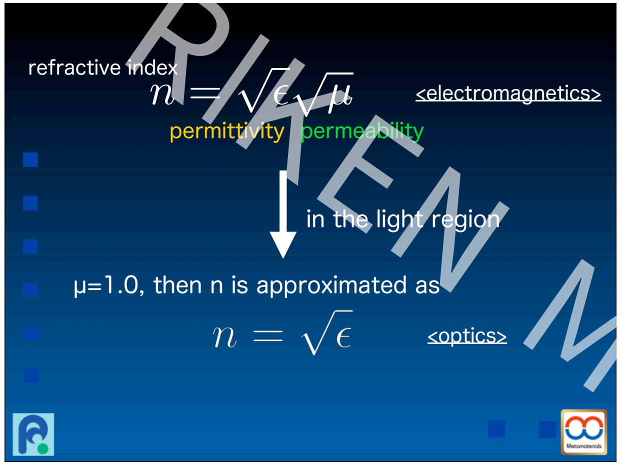


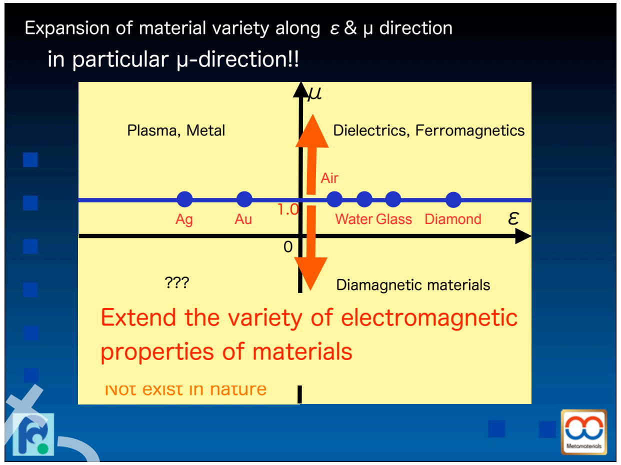
The degree of freedom of the controllability of the light propagation is limited/determined by the variety of refractive indices of materials.

In optical frequency region, all materials are only on the one line (μ=1.0).

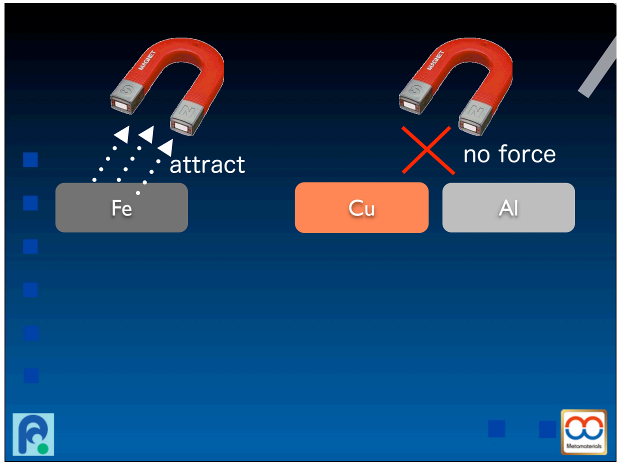


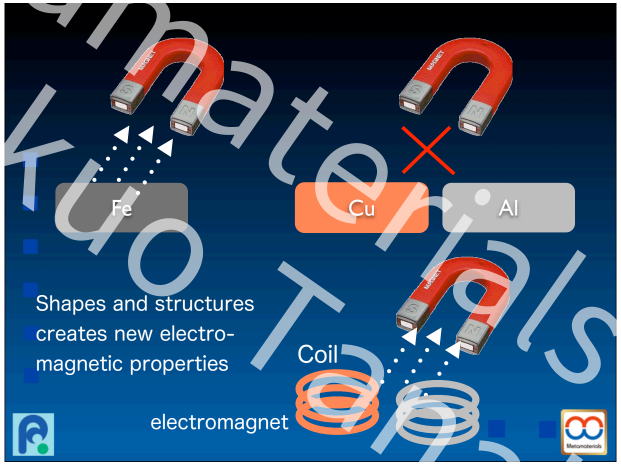


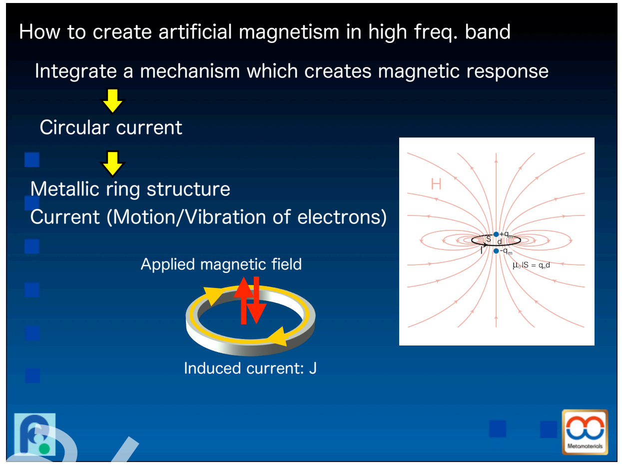

refractive index
$n = \sqrt{\epsilon}\sqrt{\mu}$
<electromagnetics>
permittivity
permeability
in the light region
μ=1.0, then n is approximated as
$n = \sqrt{\epsilon}$
<optics>

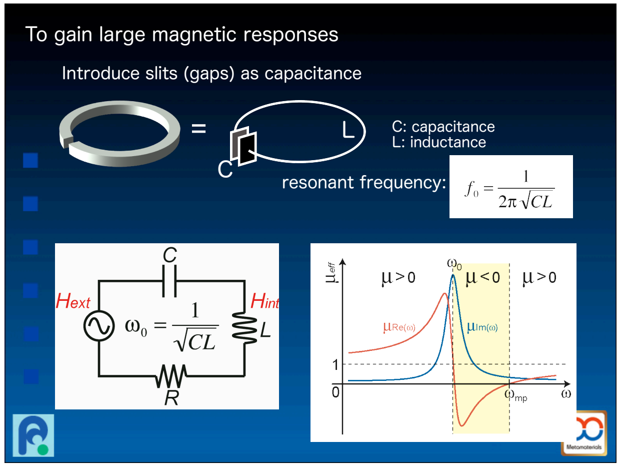

Expansion of material variety along ε & μ direction
in particular μ-direction!!
μ
Plasma, Metal
Dielectrics, Ferromagnetics
Air
1.0
Ag
Au
Water Glass
Diamond
ε
0
???
Diamagnetic materials
Extend the variety of electromagnetic properties of materials
Not exist in nature

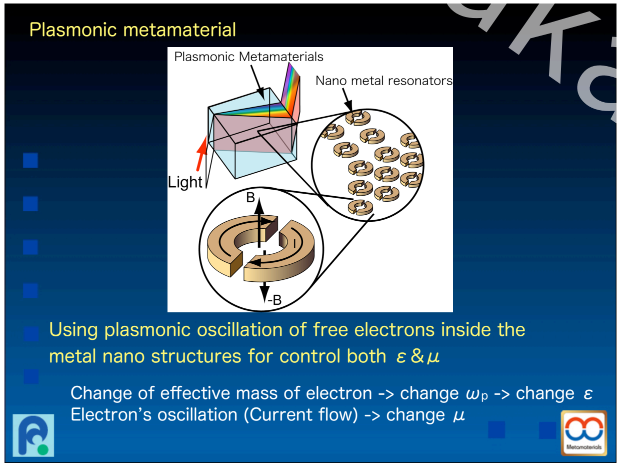

How to create magnetic material
using non-magnetic substances?

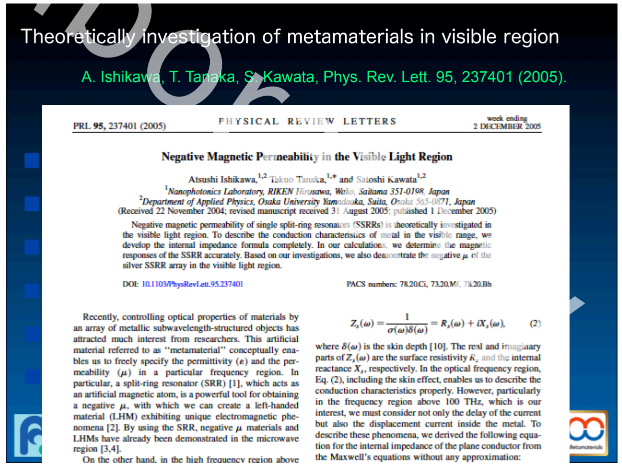

attract
no force
Fe
Cu
Al

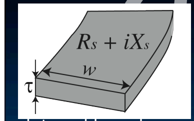

Fe
Cu
Al
Shapes and structures
creates new electro-
magnetic properties
Coil
electromagnet


How to create artificial magnetism in high freq. band
Integrate a mechanism which creates magnetic response
Circular current
Metallic ring structure
Current (Motion/Vibration of electrons)
Applied magnetic field
Induced current: J
H


To gain large magnetic responses
Introduce slits (gaps) as capacitance
=
L
C
C: capacitance
L: inductance
resonant frequency:
$f_0 = \frac{1}{2\pi\sqrt{CL}}$
C
Hext
Hint
$\omega_0 = \frac{1}{\sqrt{CL}}$
L
R
μ>0
μ<0
μ>0
ω0
1
0
ωmp
ω


Plasmonic metamaterial
Plasmonic Metamaterials
Nano metal resonators
Light
B
-B
Using plasmonic oscillation of free electrons inside the metal nano structures for control both ε & μ
Change of effective mass of electron -> change ωp -> change ε
Electron's oscillation (Current flow) -> change μ

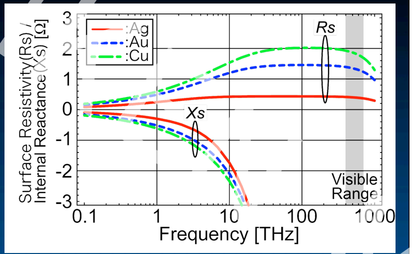

Theoretically investigation of metamaterials in visible region
A. Ishikawa, T. Tanaka, S. Kawata, Phys. Rev. Lett. 95, 237401 (2005).
PRL 95, 237401 (2005)
PHYSICAL REVIEW LETTERS
week ending 2 DECEMBER 2005
Negative Magnetic Permeability in the Visible Light Region



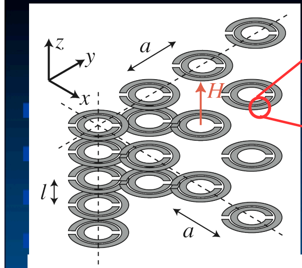
Internal Impedance

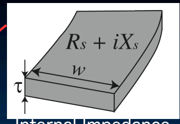
Zs = Rs + i Xs

Rs:surface resistance
Xs:internal reactance
τ :penetration depth
w :width of the ring



A. Ishikawa, T. Tanaka, S. Kawata, PRL **95**, 237401 (2005).





Internal Impedance

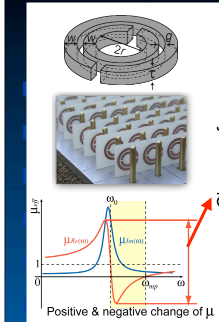
Zs = Rs + i Xs
Rs:surface resistance
Xs:internal reactance
τ :penetration depth
w :width of the ring

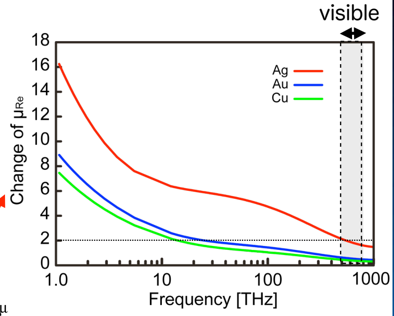
Properties of metals

$$\mu_{eff}(\omega) = 1 - \frac{F\omega^2}{\omega^2 - \frac{1}{C_g L_g} + i\frac{Z_s(\omega)\omega}{L_g}}$$

F : filling factor
Cg : geometrical capacitance
Lg : geometrical inductance
Z(ω) : impedance of the circuit

Frequency Dependence of μRe





Ag SRR exhibits Strong magnetic responses.

Rs/L : Loss
Xs/L : Dec. Fre

Increasing working frequency to visible region

Large Impedance above 100THz $f_0 = \frac{1}{2\pi\sqrt{CL}}$

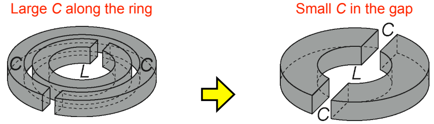
Decreasing L & C also assists the effect of large impedance.

Low resonant freq. of the SRR $\mu_{eff}(\omega) = 1 - \frac{F\omega^2}{\omega^2 - \frac{1}{CL} + i\frac{Z(\omega)\omega}{L}}$

Small *C* and large *L* is crucial
for high-freq. operation by suppressing the effect of Z(ω)

Large *C* along the ring

Small *C* in the gap

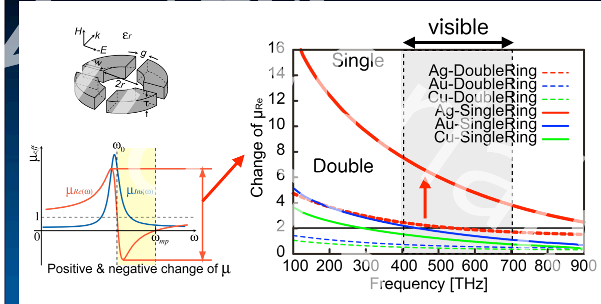


Double ring SRR

Single ring SRR

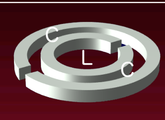
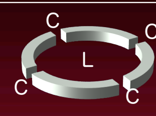
Frequency Dependence of μRe

for *F* = 6.41%
εr = 2.25 (e.g. glass)
w = τ = 2.5 δ(ω)



J. Opt. Soc. Am. B, **24**, 510 (2007).

Design strategy of nano-resonator

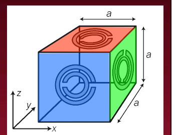
frequency	~ 100THz	100THz ~
structure	 double ring SRR	 single ring SRR
required	large *C* & wide ring	small *C* & large L
resonant frequency	$f_0 = \frac{1}{2\pi\sqrt{CL}}$	$f_0 < \frac{1}{2\pi\sqrt{CL}}$
magnetic response	decreased due to resistance: *Rs*	saturation due to the decrease of *L*

How to make?

Requirements for metamaterials

1. plasmonic material
   low resistivity (good conductor) -> metal

2. resonator with high Q-value
   shape shoud be well designed
   resonant frequency -> C, L



3. Array
   Three-dimensional array structure

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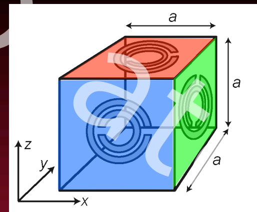
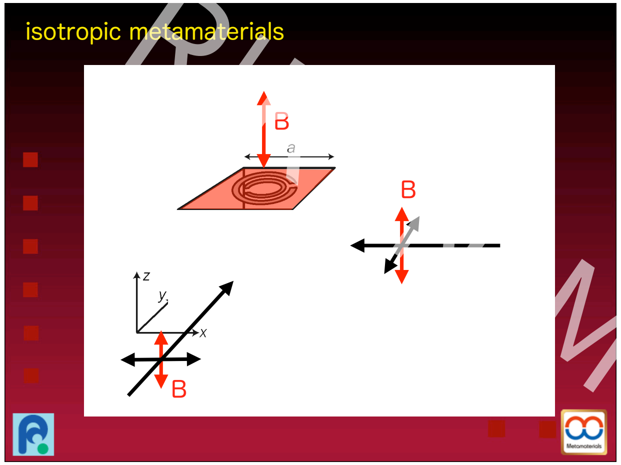
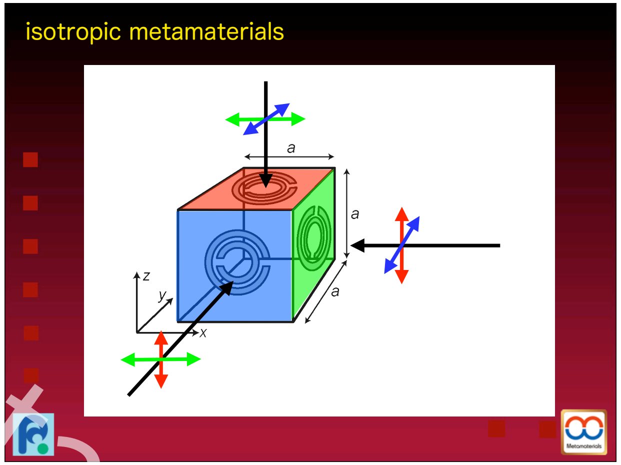
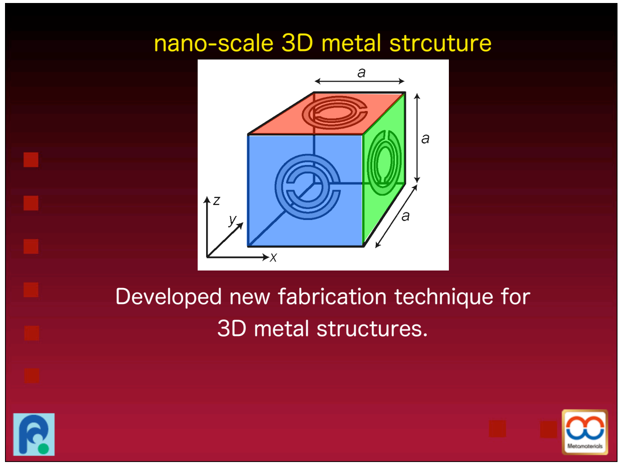
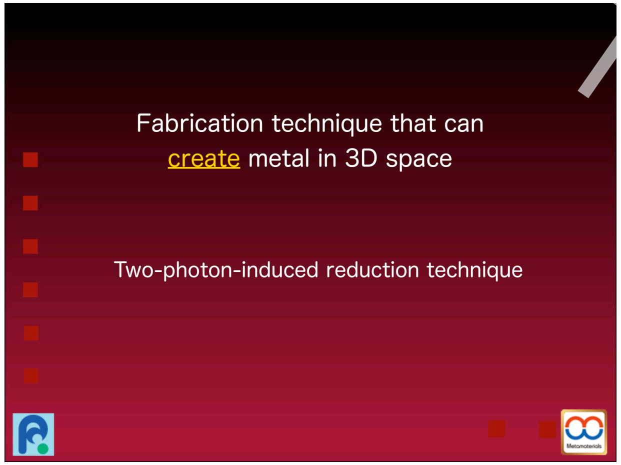
isotropic metamaterials

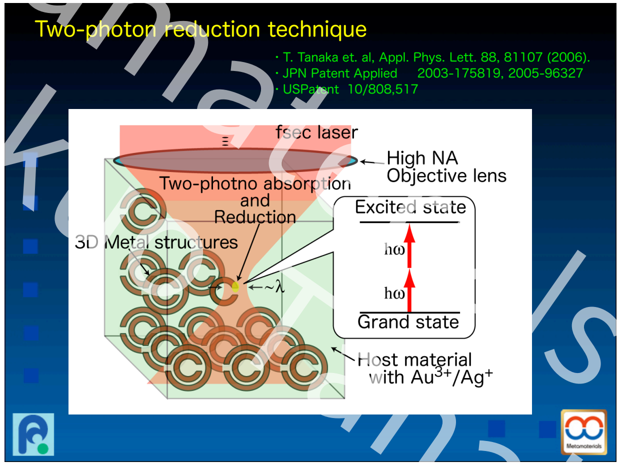


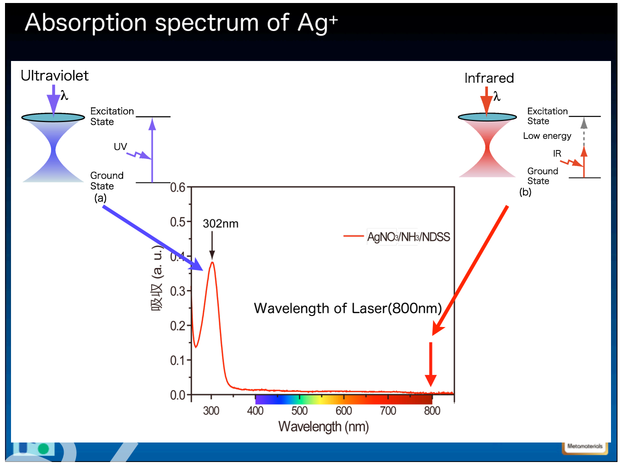

isotropic metamaterials
B
a
B
z
y
x
B

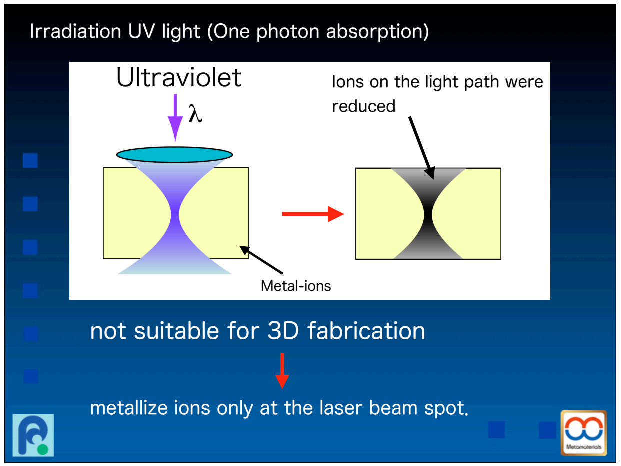

isotropic metamaterials
a
a
a
z
y
x

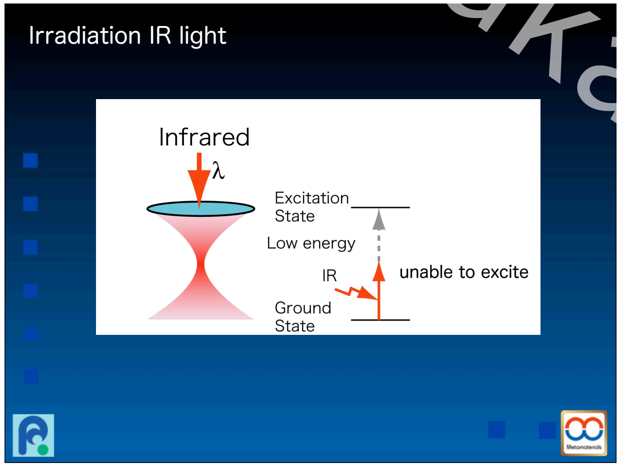

nano-scale 3D metal strcuture
a
a
a
z
y
x
Developed new fabrication technique for
3D metal structures.

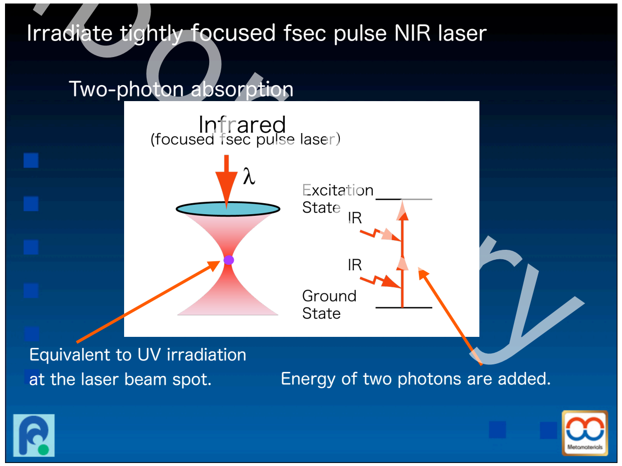

Fabrication technique that can
create metal in 3D space
Two-photon-induced reduction technique

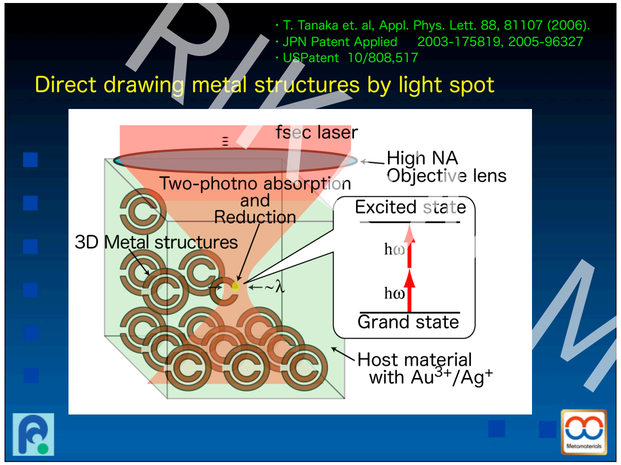

Two-photon reduction technique
· T. Tanaka et. al, Appl. Phys. Lett. 88, 81107 (2006).
· JPN Patent Applied 2003-175819, 2005-96327
· USPatent 10/808,517
fsec laser
High NA
Objective lens
Two-photno absorption
and
Reduction
3D Metal structures
Excited state
hω
hω
Grand state
Host material
with Au3+/Ag+

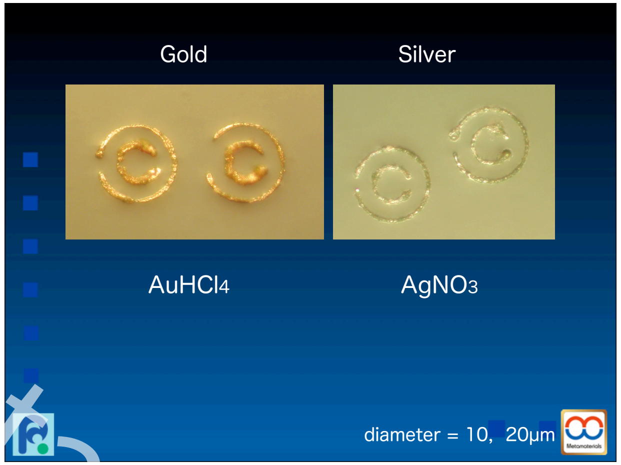

Absorption spectrum of Ag+
Ultraviolet
λ
Excitation
State
UV
Ground
State
(a)
Infrared
λ
Excitation
State
Low energy
IR
Ground
State
(b)
302nm
AgNO3/NH3/NDSS
Wavelength of Laser(800nm)
吸収 (a. u.)
Wavelength (nm)

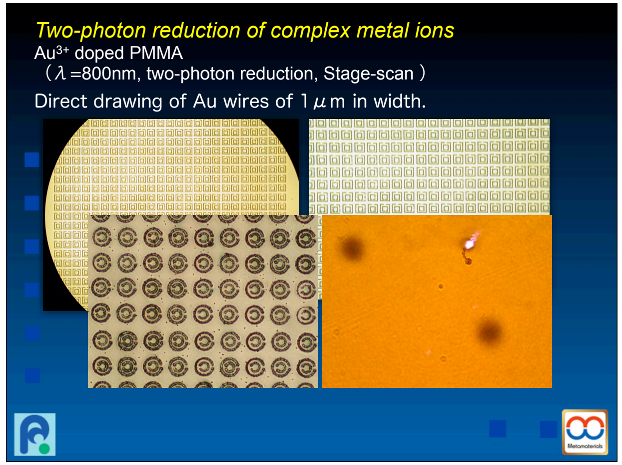

Irradiation UV light (One photon absorption)
Ultraviolet
λ
Ions on the light path were
reduced
Metal-ions
not suitable for 3D fabrication
metallize ions only at the laser beam spot.

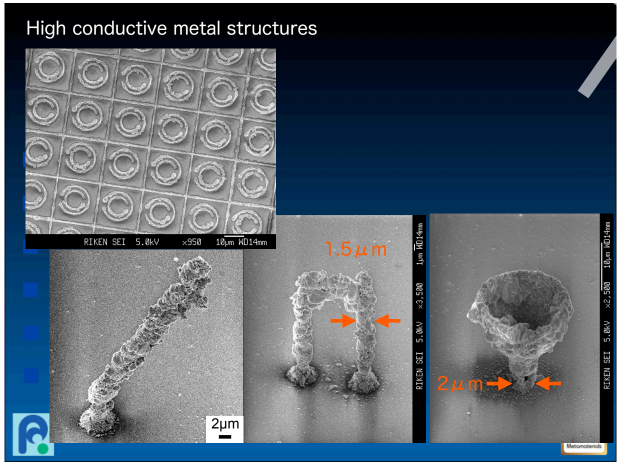

Irradiation IR light
Infrared
λ
Excitation
State
Low energy
IR
unable to excite
Ground
State

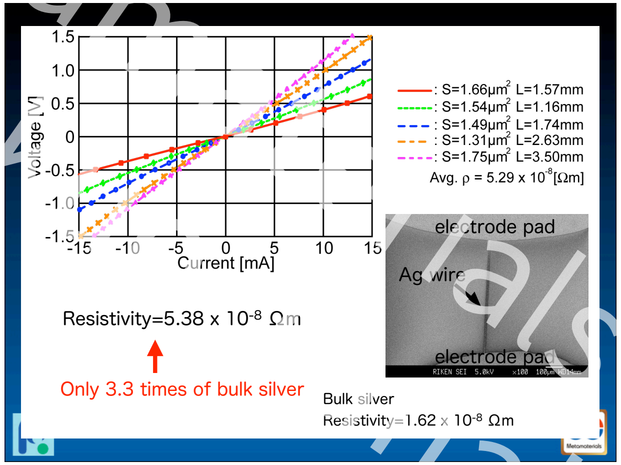

Irradiate tightly focused fsec pulse NIR laser
Two-photon absorption
Infrared
(focused fsec pulse laser)
λ
Excitation
State
IR
IR
Ground
State
Equivalent to UV irradiation
at the laser beam spot.
Energy of two photons are added.

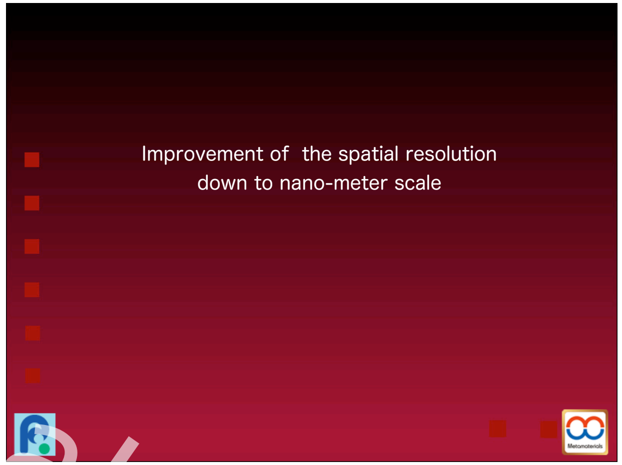

· T. Tanaka et. al, Appl. Phys. Lett. 88, 81107 (2006).
· JPN Patent Applied 2003-175819, 2005-96327
· USPatent 10/808,517
Direct drawing metal structures by light spot
fsec laser
High NA Objective lens
Two-photno absorption and Reduction
Excited state
3D Metal structures
hω
hω
Grand state
Host material with Au^{3+}/Ag^{+}

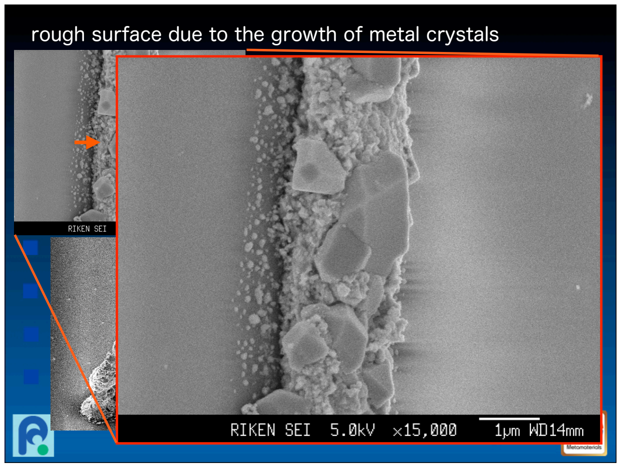

Gold
Silver
$AuHCl_4$
$AgNO_3$
diameter = 10, 20μm

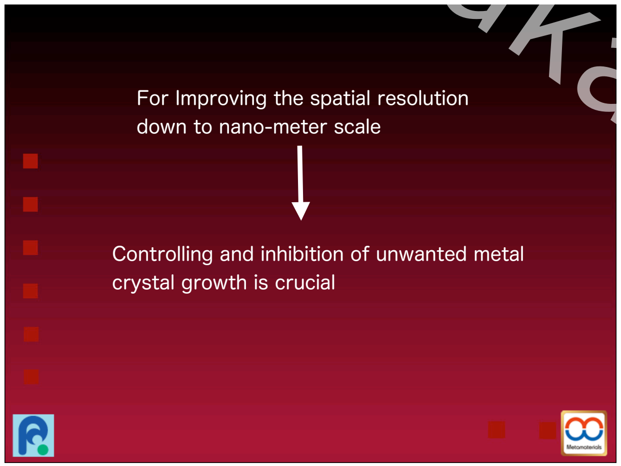

Two-photon reduction of complex metal ions
Au^{3+} doped PMMA
(λ=800nm, two-photon reduction, Stage-scan)
Direct drawing of Au wires of 1μm in width.

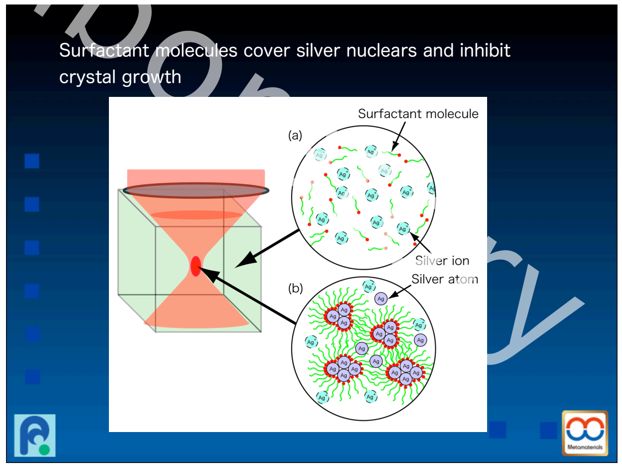

High conductive metal structures
1.5μm
2μm
2μm

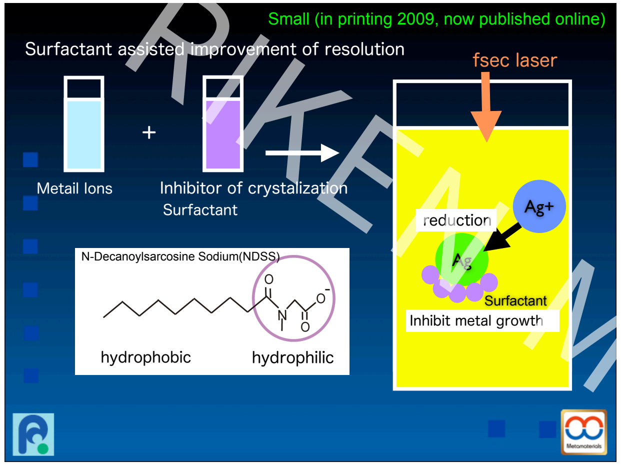

Voltage [V]
Current [mA]
: S=1.66μm^2 L=1.57mm
: S=1.54μm^2 L=1.16mm
: S=1.49μm^2 L=1.74mm
: S=1.31μm^2 L=2.63mm
: S=1.75μm^2 L=3.50mm
Avg. ρ = 5.29 x 10^{-8} [Ωm]
electrode pad
Ag wire
electrode pad
Resistivity=5.38 x 10^{-8} Ωm
Only 3.3 times of bulk silver
Bulk silver
Resistivity=1.62 x 10^{-8} Ωm

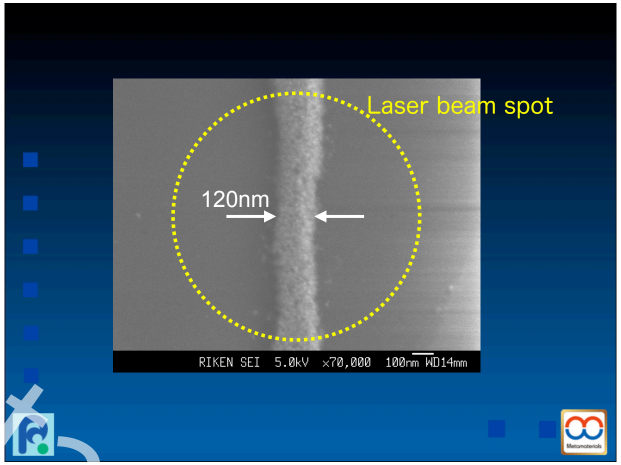

Improvement of the spatial resolution
down to nano-meter scale

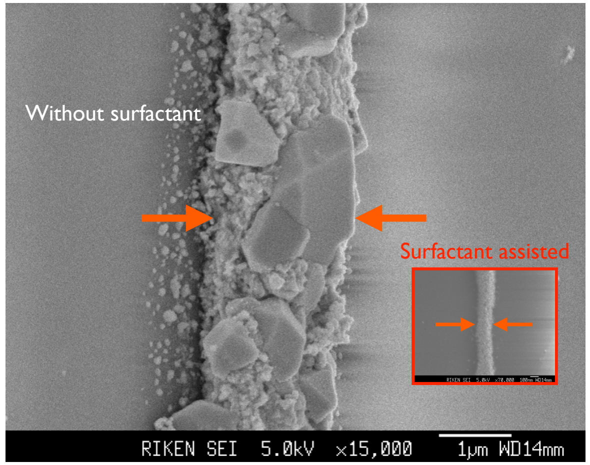

rough surface due to the growth of metal crystals
RIKEN SEI 5.0kV ×15,000 1μm WD14mm

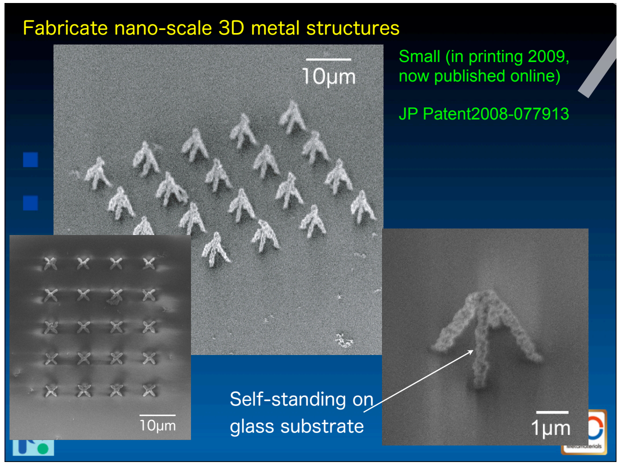

For Improving the spatial resolution
down to nano-meter scale
Controlling and inhibition of unwanted metal
crystal growth is crucial

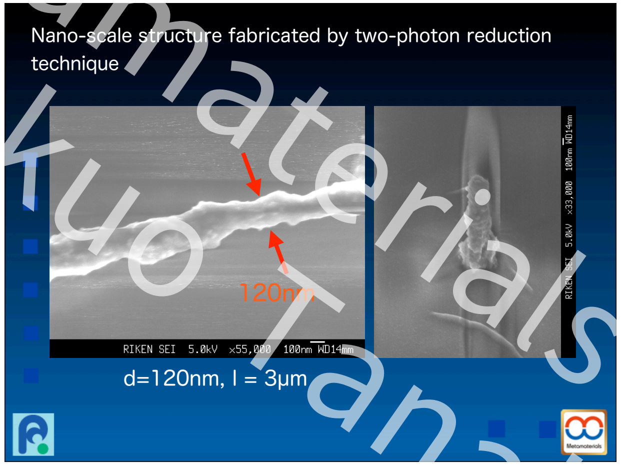

Surfactant molecules cover silver nuclears and inhibit
crystal growth
Surfactant molecule
(a)
(b)
Silver ion
Silver atom

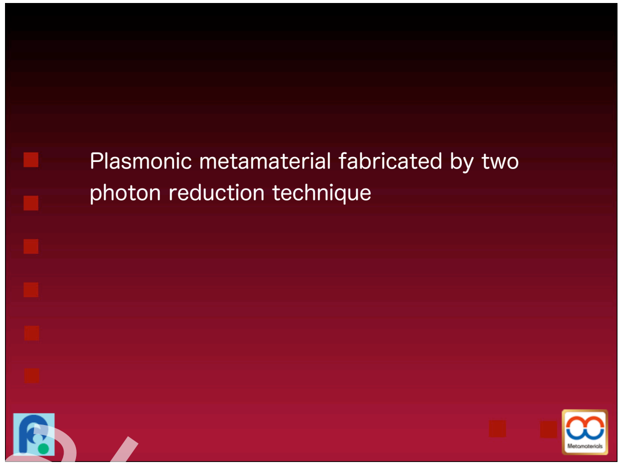

Small (in printing 2009, now published online)
Surfactant assisted improvement of resolution
fsec laser
Metail Ions
+
Inhibitor of crystalization
Surfactant
N-Decanoylsarcosine Sodium(NDSS)
hydrophobic
hydrophilic
reduction
Ag+
Ag
Surfactant
Inhibit metal growth

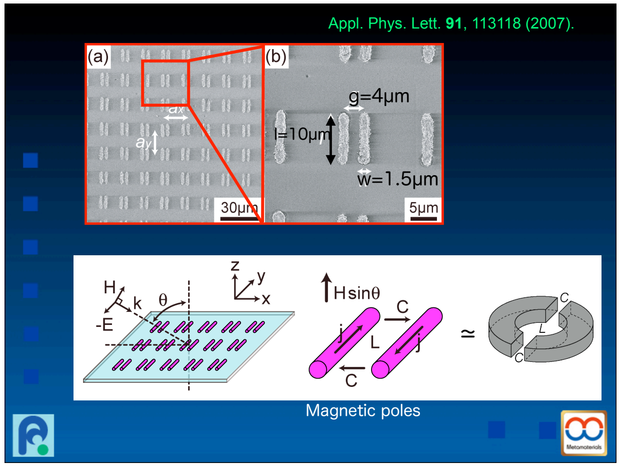

Laser beam spot
120nm
RIKEN SEI 5.0kV ×70,000 100nm WD14mm

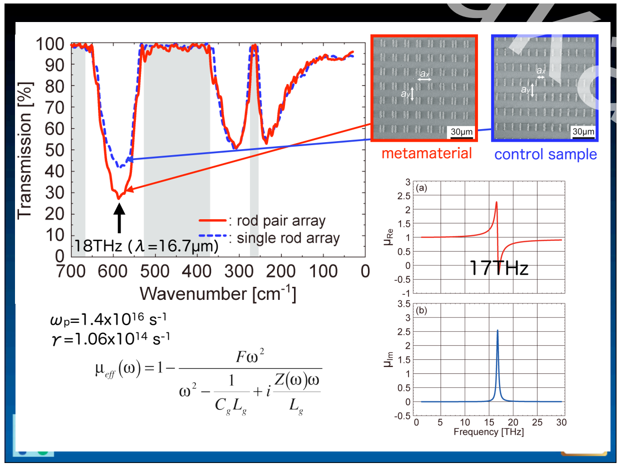

Without surfactant
Surfactant assisted
RIKEN SEI 5.0kV ×15,000 1μm WD14mm

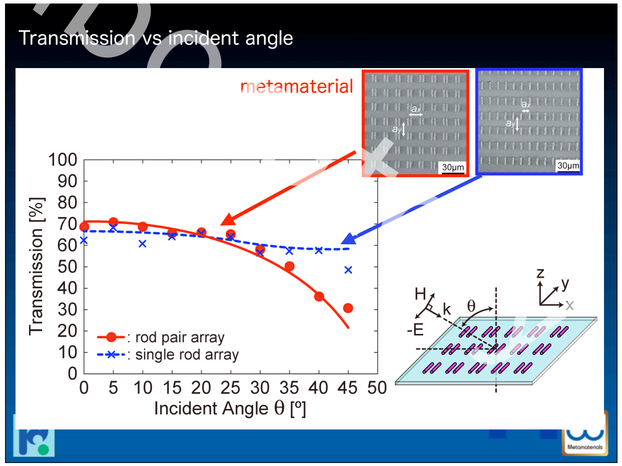

Fabricate nano-scale 3D metal structures
10μm
Small (in printing 2009, now published online)
JP Patent2008-077913
10μm
Self-standing on glass substrate
1μm


Nano-scale structure fabricated by two-photon reduction technique
120nm
RIKEN SEI 5.0kV ×55,000 100nm WD14mm
d=120nm, l = 3μm

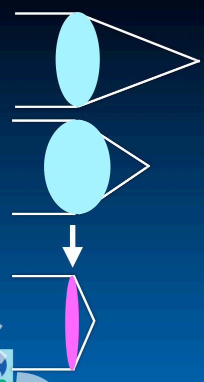

Plasmonic metamaterial fabricated by two photon reduction technique


Appl. Phys. Lett. 91, 113118 (2007).
(a)
(b)
g=4μm
l=10μm
w=1.5μm
30μm
5μm
Hsinθ
Magnetic poles


Transmission [%]
Wavenumber [cm-1]
18THz (λ=16.7μm)
rod pair array
single rod array
metamaterial
control sample
17THz
Frequency [THz]
ωp=1.4x10^16 s-1
γ=1.06x10^14 s-1
μeff(ω)=1−Fω²/(ω²−1/(CgLg)+iZ(ω)ω/Lg)


Transmission vs incident angle
metamaterial
Transmission [%]
rod pair array
single rod array
Incident Angle θ [º]

A simple applications of plasmonic metamaterials




屈折率高めレンズ薄く

メガネ・カメラに応用

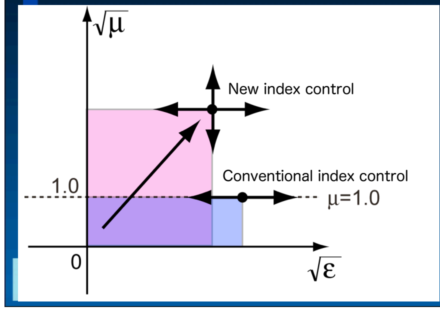
理研　透明材料にリング状金属

Nikkei Business Daily 2007/4/18 Page. 11

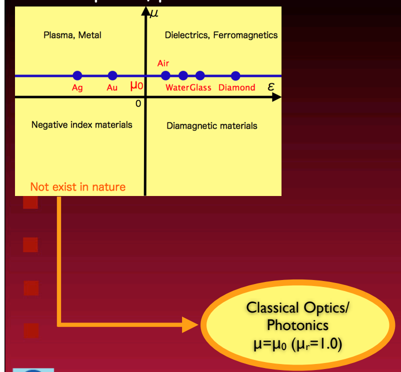
New refractive index control

$$n = \sqrt{\epsilon}\sqrt{\mu}$$

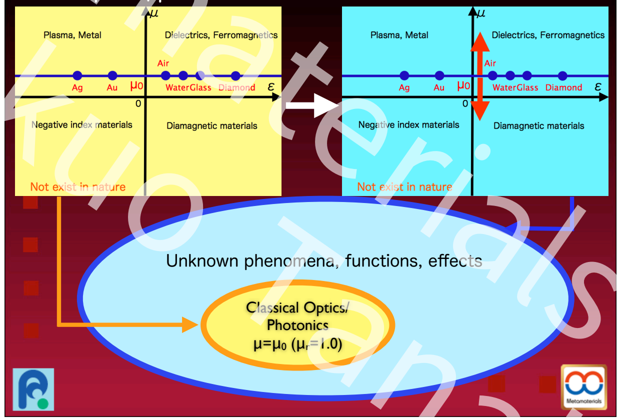
n=1.76, ε=3.10, μ=1.0 → +0.12 (x1.023) → n=1.80, ε=3.24, μ=1.046 ($(1.023)^2$)



New optics/photonics world



New optics/photonics world



Conclusion

- Brief introduction of plasmonic metamaterials
- Fabrication techniques for metamaterials
  3D metal structures with nano-scale resolution
  Two-photon reduction technique.
  Inhibition of unwanted crystallization of metal is crucial
- Megnetically excited magnetic response of metamaterials fabricated by two-photon reduction technique.