Novel EO Materials

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- Fabrication, characterisation & processing of metal-glass nanocomposites for storage of information, sensing, circuitry, security, and production of diffractive optical elements;
- Laser micro/nano processing of metals and composites for applications in surface engineering, energy sector, healthcare and creative industries;
- Studies of a novel crystal optics phenomenon (conical diffraction) for applications in photonics and image processing.

Original idea came from a discussion paper at DESY by Kirsten Hacker …

Percolation Film as a Replacement for the Electro-optical Crystal in Longitudinal Profile Measurements of Short Particle Bunches

K. Hacker

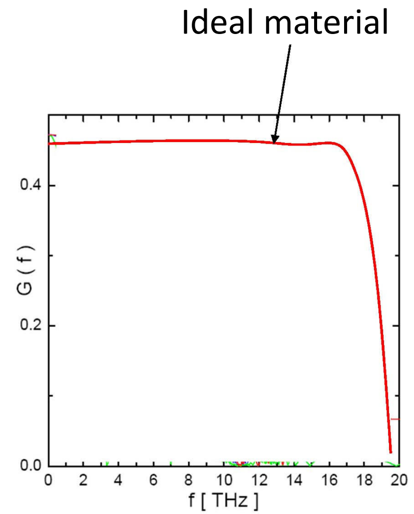
16-06-10

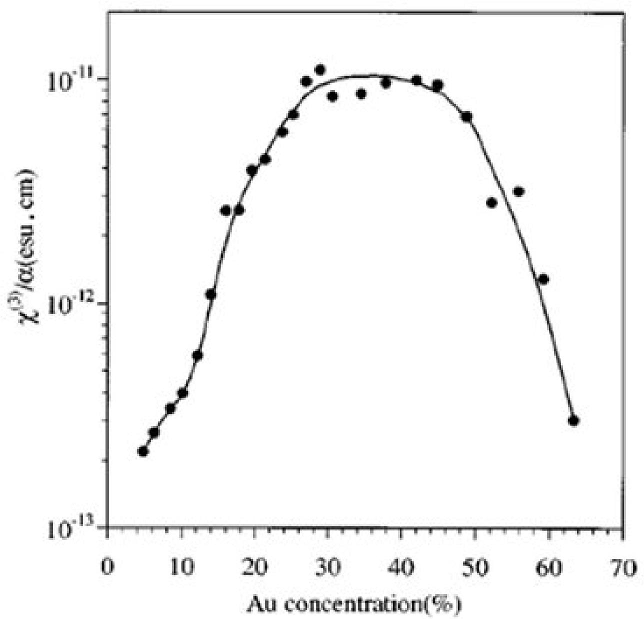
DESY Ideenmarkt

Ideal Material: thin film with strong EO effect, a 2-D birefringent crystal

- No more transverse oscillations

- No more worries about phase matching laser pulse and e-beam field



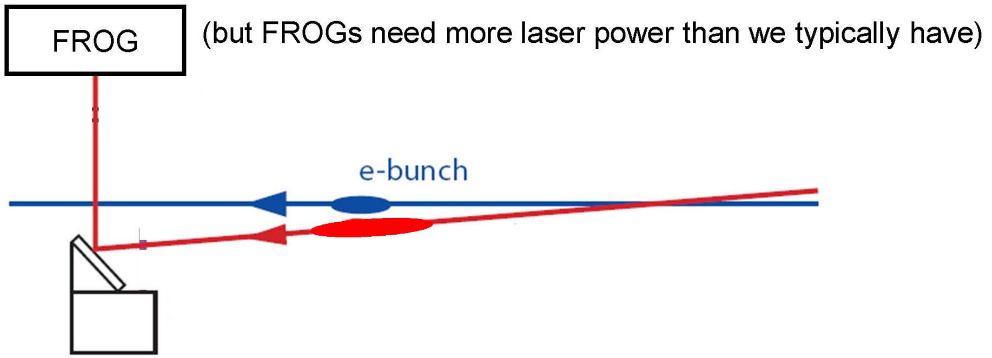


- AuSi percolation films demonstrate several nonlinear behaviours:

Concerns about Percolation Films

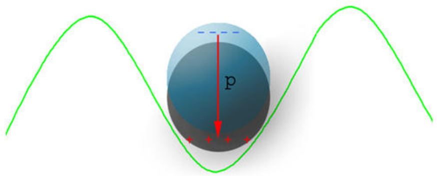
- Each film is unique
- Optical properties vary with laser beam position => spatial decoding may be spiky
- Reflected spectrum will be broadband, but somewhat "spiky"
  - If laser spot size is large, spiky-ness could be averaged out
  - Alternatively, one could focus the laser beam on a single resonant location
- Film degredation (melting?!)
- Film response time/relaxation time?
- Films not yet characterized out to 20 THz.. just theory

Or..? -Use long, chirped laser pulses and Frequency Resolved Optical Gating



Intrigued by these ideas, we decided to attempt to make "metamaterials" using silver nanoparticles embedded in a dielectric (glass or polymer).

This required setting up at Dundee University new laboratories for laser processing of MDNs and metals.



Lycurgus cup
(*4th century AD*)
Roman art in the British Museum.

+ stained-glass windows in cathedrals

Mie theory for scattering & absorption of light by spheres

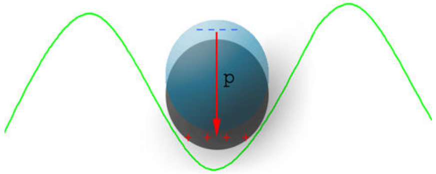
Polarizability ***α*** and induced dipole moment ***p*** of a metal sphere embedded in a dielectric are given by:

$$\alpha = 4\pi R^3 \frac{\varepsilon_i(\omega) - \varepsilon_h}{\varepsilon_i(\omega) + 2\varepsilon_h}$$

$$\vec{p}(\omega) = \alpha\varepsilon_0 \vec{E}_0(\omega) = 4\pi\varepsilon_0 R^3 \frac{\varepsilon_i(\omega) - \varepsilon_h}{\varepsilon_i(\omega) + 2\varepsilon_h} \vec{E}_0(\omega)$$

R	Radius of the nanoparticle
$\varepsilon_i(\omega)$	Complex permittivity of the metal
ε_h	Complex permittivity of the host matrix
E_0	Electric field strength of the incident electromagnetic wave
ε_0	Permittivity of vacuum

- Michael Faraday, Phil. Trans. Royal Society **147**, 145 (1857).
- Gustav Mie, Ann. Phys. (Leipzig) **25**, 377 (1908).
- Kreibig, U & Volmer, M. Optical Properties of Metal Clusters, Springer (1995).



The absorption cross-section of a spherical metal inclusion placed in a transparent dielectric matrix (Im[ε_h]→0)

$$\sigma(\omega) = 12\pi R^3 \frac{\omega}{c} \varepsilon_h^{3/2} \frac{\varepsilon_i''(\omega)}{\left[\varepsilon_i'(\omega) + 2\varepsilon_h\right]^2 + \varepsilon_i''(\omega)^2}$$

Real & **Imaginary** parts of the electric permittivity of the metal

$\varepsilon_i(\omega)$ can be described by the ***Drude-Sommerfeld*** relationship $\varepsilon_i(\omega) = \varepsilon_b + 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}$

- ε_b Complex electric permittivity associated with inter-band transitions of the core electrons in the atom
- γ Damping constant of the electron oscillations
- ω_p Free-electron plasma frequency
- N Density of the free electrons
- m Effective mass of electron

$$\omega_p = \sqrt{\frac{Ne^2}{m\varepsilon_0}}$$

The **Mie resonance** occurs at the surface plasmon (SP) frequency $\boldsymbol{\omega_{SP}}$ when:

$$\left[\varepsilon_i'(\omega) + 2\varepsilon_h\right]^2 + \varepsilon_i''(\omega)^2 \rightarrow Minimum$$

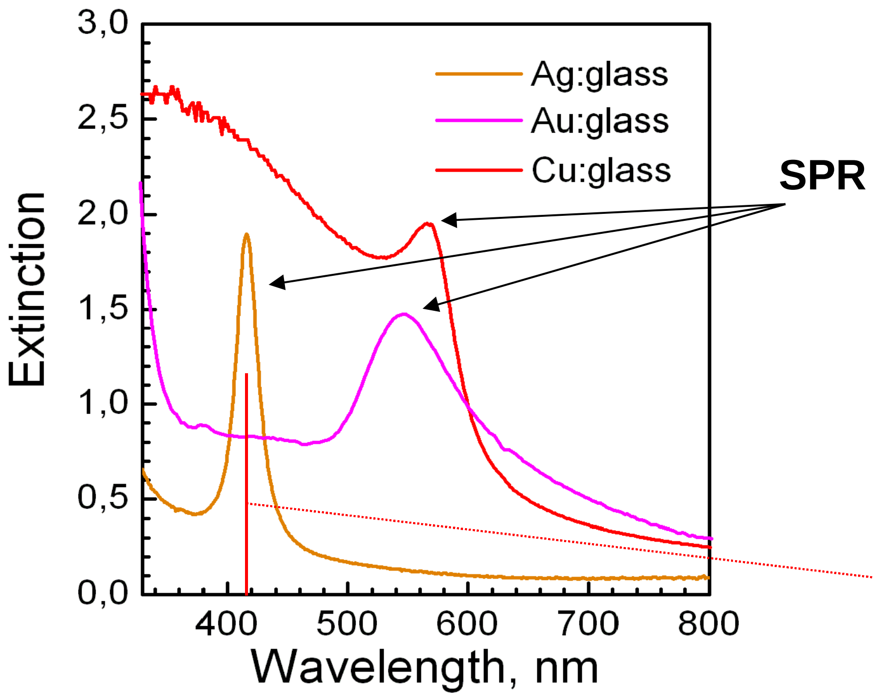
$$\varepsilon_i'(\omega_{SP}) = -2\varepsilon_h$$

Bohren, C. F.; Huffman, D. R. Absorption & Scattering by Small Particles; Wiley (1983).

Core electrons define the position of the SPR in the extinction spectra of different noble metals.

Absorption (Extinction) spectra of glass containing spherical **Silver**, **Gold** & **Copper** nanoparticles.

$$\omega_{SP}^2 = \frac{\omega_p^2}{\mathrm{Re}[\varepsilon_b] + 1 + 2\varepsilon_h} - \gamma^2$$



ω_{SP} SPR frequency
ω_P Free-electron plasma frequency
γ Damping constant of the electron oscillation
ε_b Complex electric permittivity of inter-band transitions of the core electrons in the atoms
ε_h Complex electric permittivity of the host matrix

silver peaks at around 420 nm

- Kreibig, U & Volmer, M. Optical Properties of Metal Clusters. Springer (1995).
- Bohren, C. F.; Huffman, D. R. Absorption & Scattering by Small Particles. Wiley (1983).

SP position is size dependent, therefore metal nanoparticles with non-spherical shape should demonstrate several SPR in their spectra

$$\alpha_k(\omega) = \frac{4\pi}{3} abc \frac{\varepsilon_i(\omega) - \varepsilon_h}{\varepsilon_h + \left(\varepsilon_i(\omega) + \varepsilon_h\right) L_k}$$

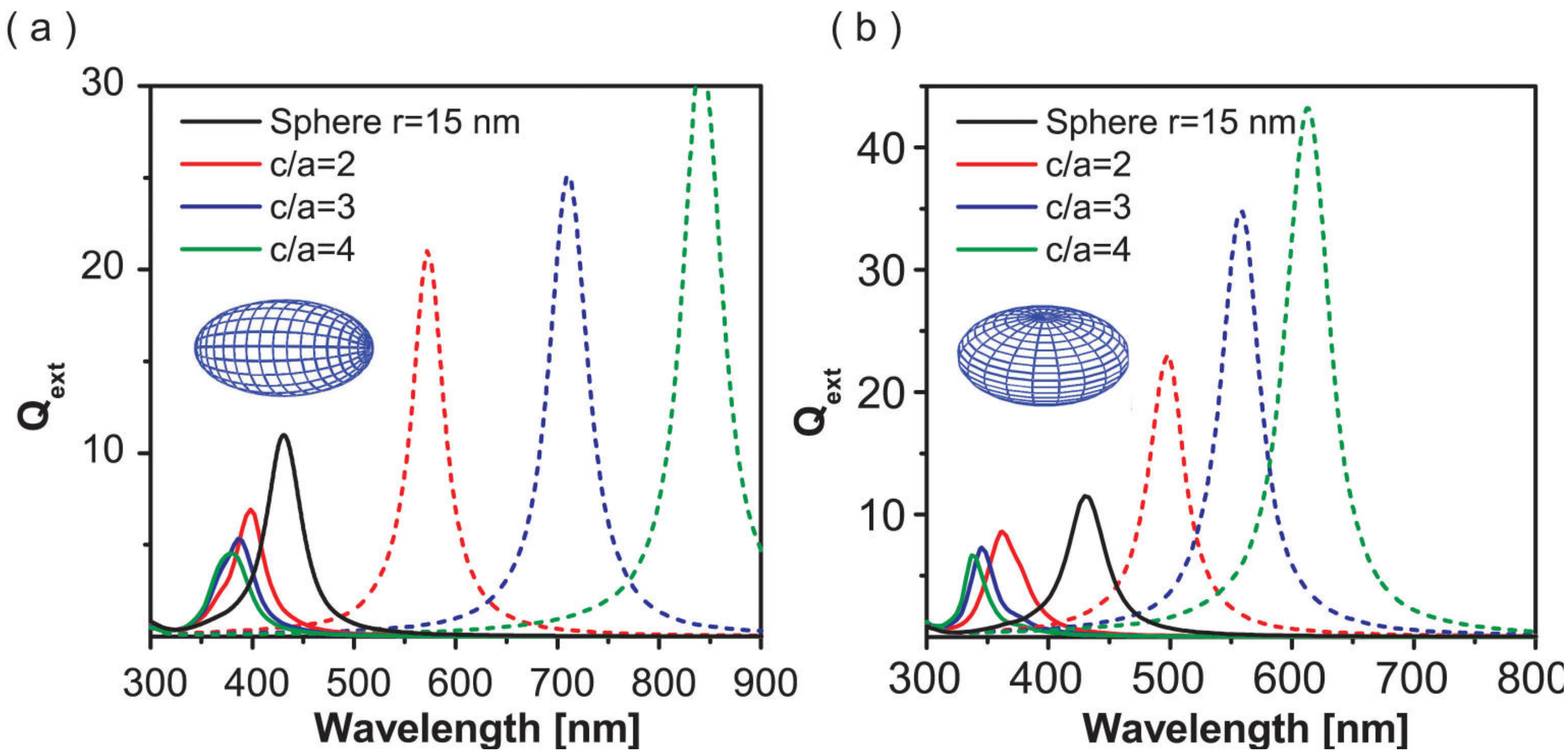
- L_K is the geometrical depolarization factor for each axis $\Sigma L_k = 1$;
- Increase in the axis length leads to the minimization of the depolarization factor.
- **Spherical** particles: a = b = c ⇒ spectrum exhibits **one** SP mode.
- **Spheroidal** particles: a ≠ b = c ⇒ spectrum exhibits **two** SP modes corresponding to polarizabilities along principal axes*
- **Ellipsoidal** particles: a ≠ b ≠ c ⇒ spectrum exhibits **three** SP modes corresponding to polarizabilities along principal axes.

* *If the incident light is polarized parallel to one of the axes, only one single SP band corresponding to the appropriate axis is observed*

• Kreibig, U & Volmer, M. Optical Properties of Metal Clusters. Springer (1995).

Mie theory for silver spheroids embedded in glass - with different aspect ratios

Polarization extinction spectra for (a) **prolate** and (b) **oblate** silver spheroids



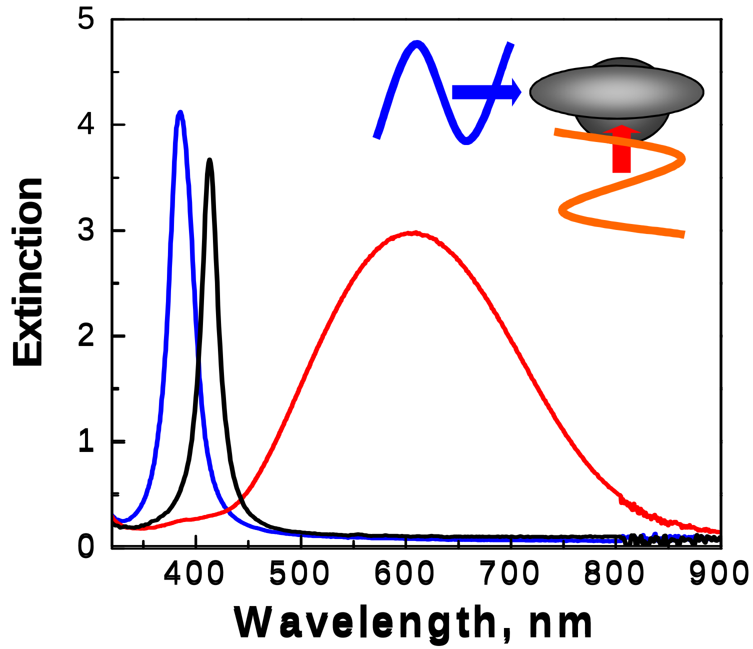
- Volume of spheroids is equal to the volume of a nanosphere with radius 15 nm;
- **Dashed curves:** polarization of the light is **parallel** to the **long axis**;
- **Solid curves:** polarization of the light is **parallel** to the **short axis**.

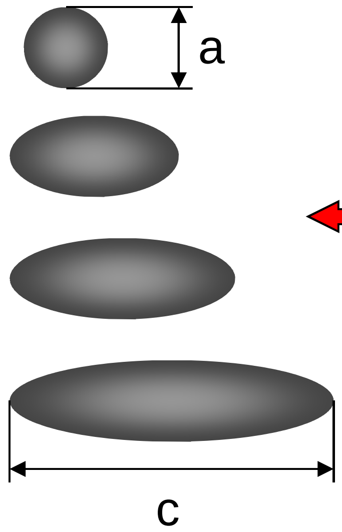
Astrophys. Space Sci. **204**, 19 (1993).

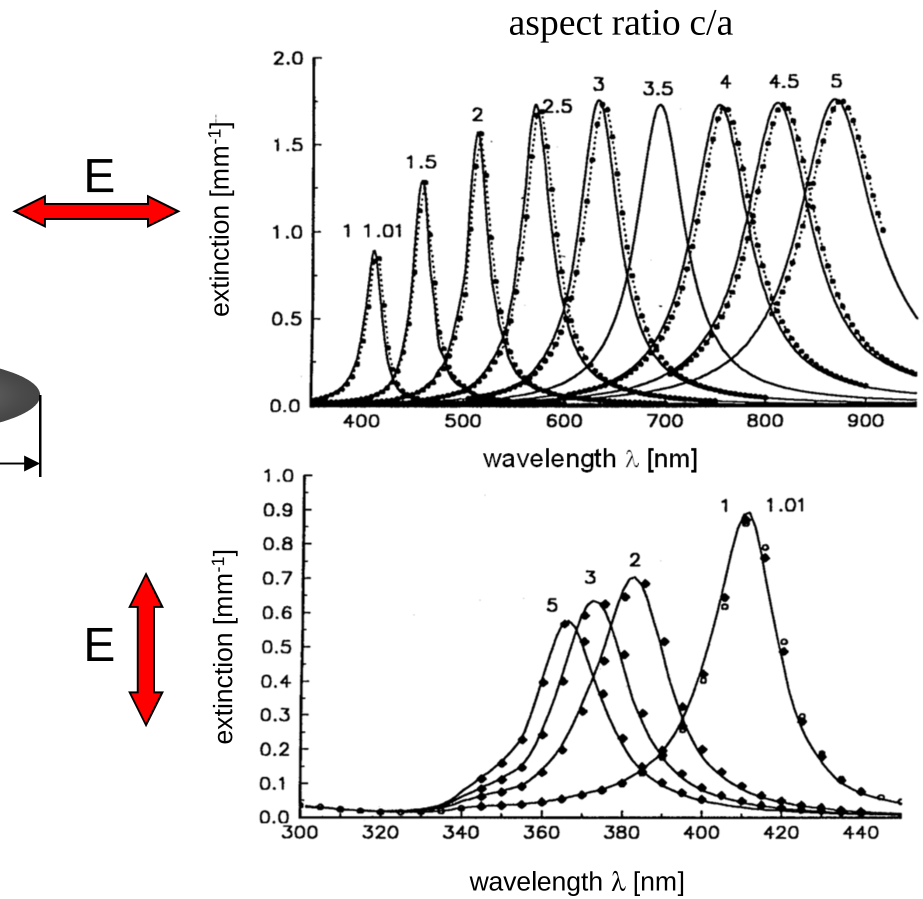
Optical properties of glass with embedded metallic particles

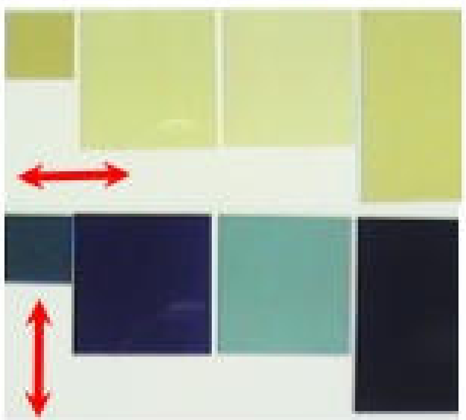
Polarized extinction spectra of spherical & spheroidal silver particles in glass

Increase in aspect ratio leads to rise of spectral gap between SPRs in polarized spectra

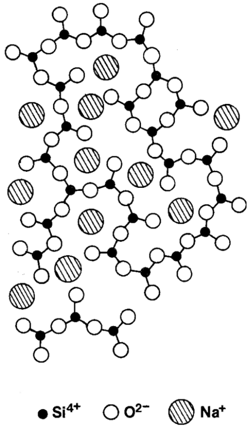


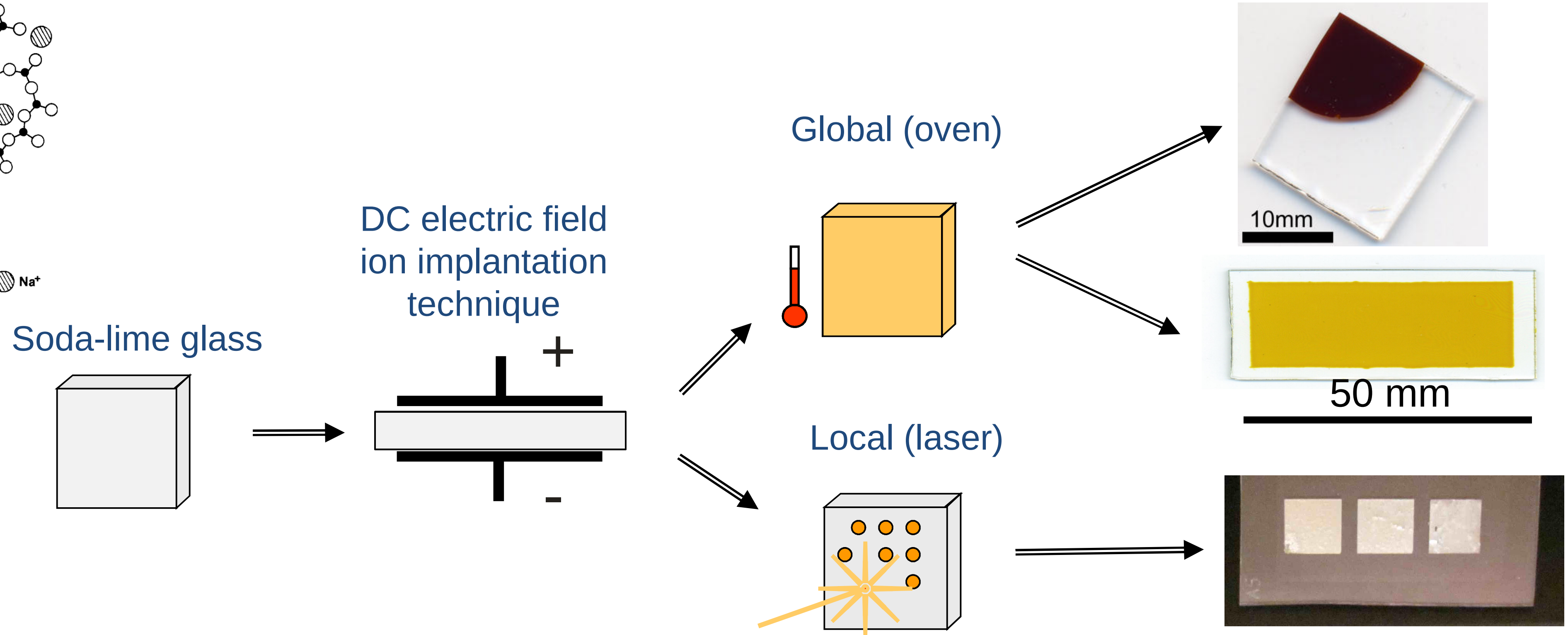






DC electric field-assisted ion exchange & reduction in air or by laser





Reduction mechanisms

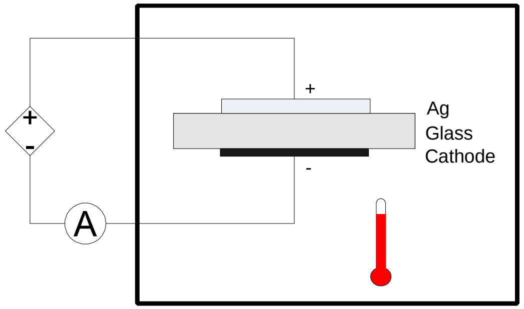
$$2\left(\equiv Si-O^{-}Ag^{+}\right)\leftrightarrow\equiv Si-O-Si\equiv+O^{1-}+(Ag_{2})^{1+}$$

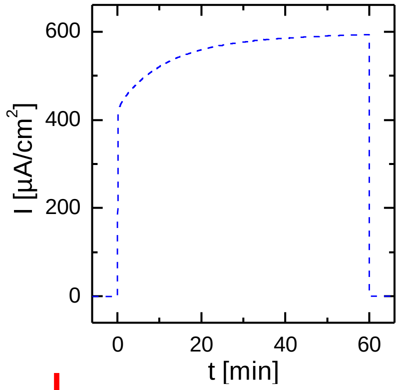
$$2O^{1-}+2Ag^{1+}\leftrightarrow 2Ag^{0}+O_{2}$$

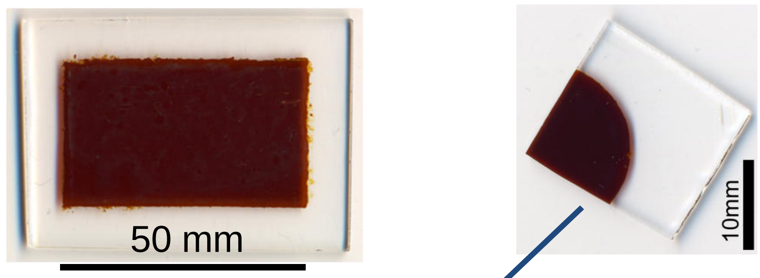
$$Ag^{+}+Ag^{+}\rightarrow Ag^{2+}+Ag^{0}$$

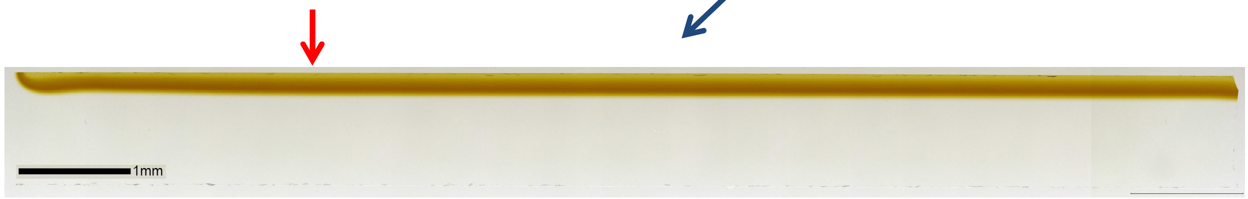
Optical Mater. Express **1**, 1224 (2011).

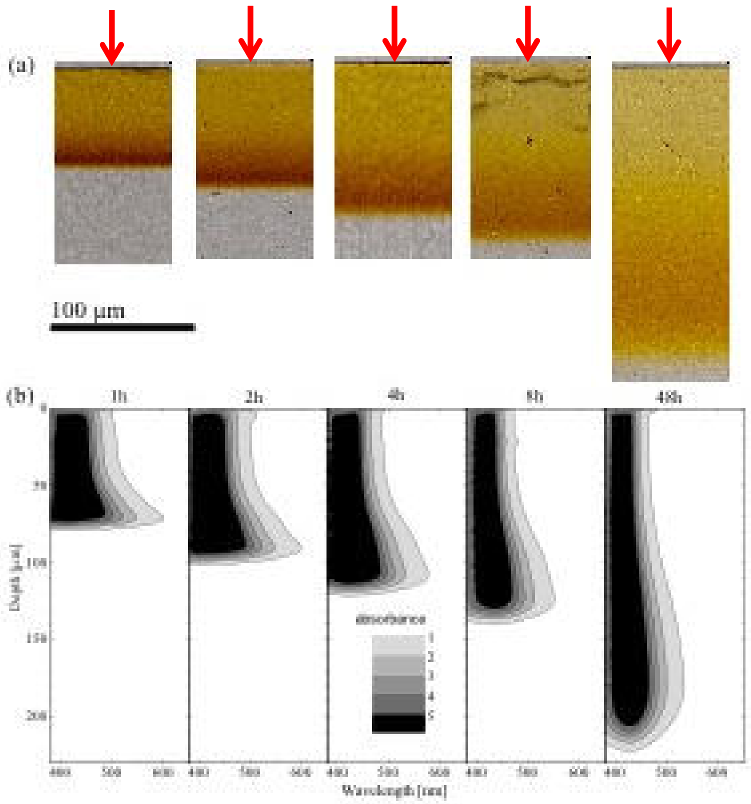
Fabrication of glass with high fraction of embedded metallic particles









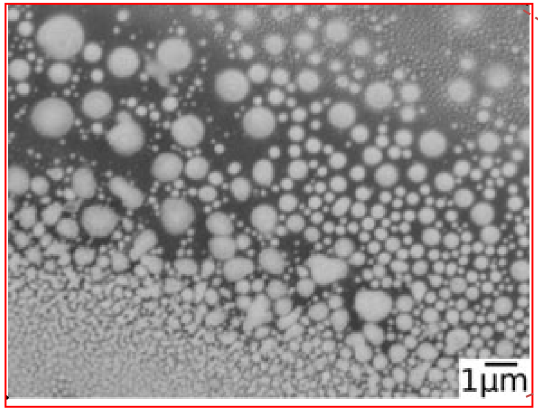


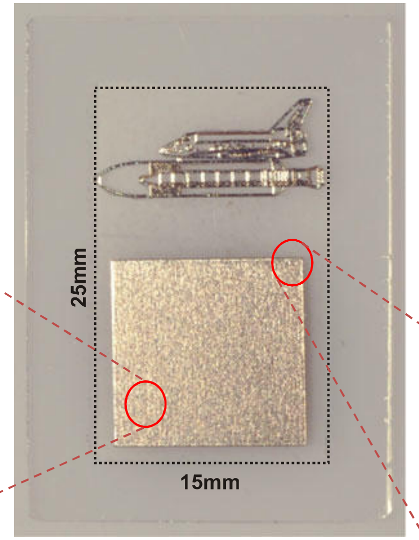
- Control over the size of the produced embedded nanoparticles **(2 nm - 50nm in diameter)**
- Control over the thickness of the nanoparticle-containing layer in glass **(500 nm - 250 µm).**
- Control over the spatial distribution (filling factor) of the nanoparticle-containing layer

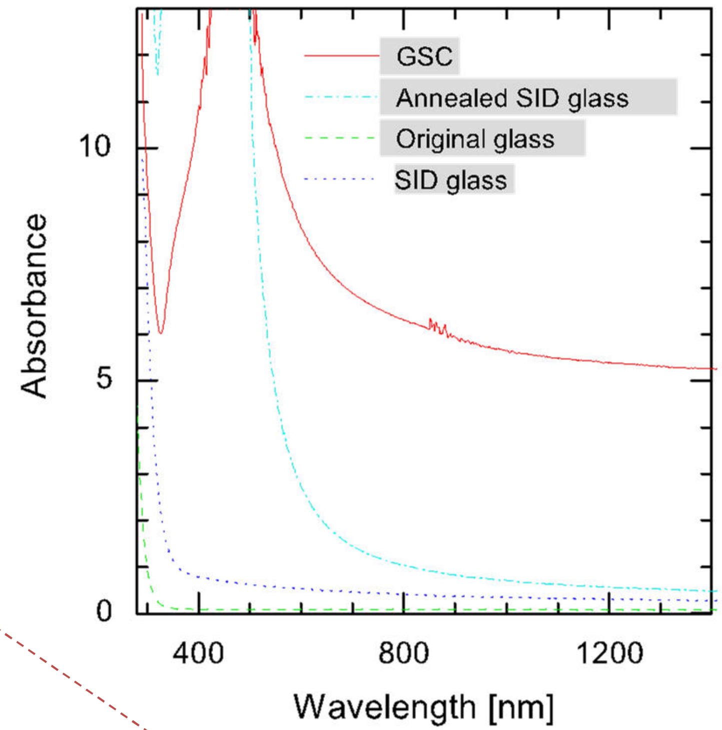
- Optical Mater. Express **1**, 1224 (2011).
- Optics Express **20**, 23227 (2012).

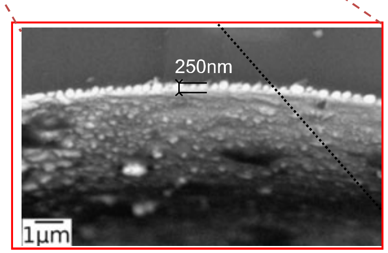
Nanosecond-pulsed laser irradiation of silver-ion doped glass

- Wavelength: **355 nm**
- Pulse length ~ **8 ns** at 80 kHz
- Laser fluence ~ 420 mJ/cm^2
- Beam spot diameter ~ 60 µm
- Writing speed: **14 mm/s**
- ~ 330 pulses per spot



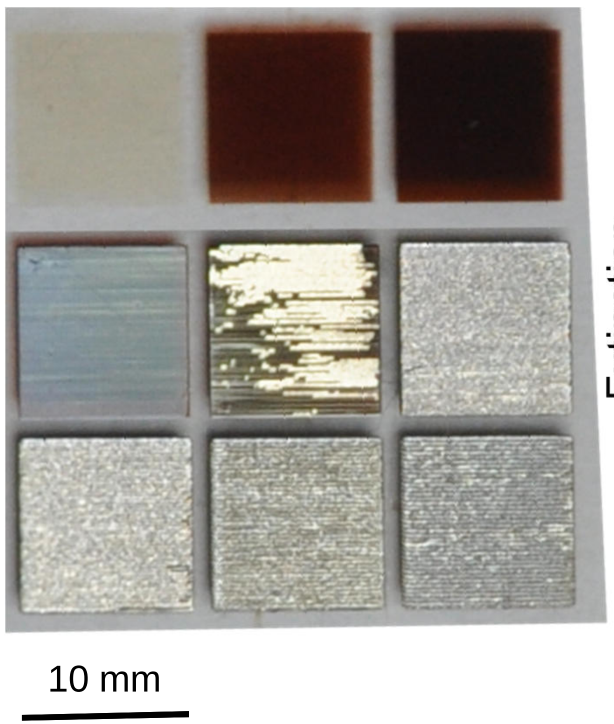


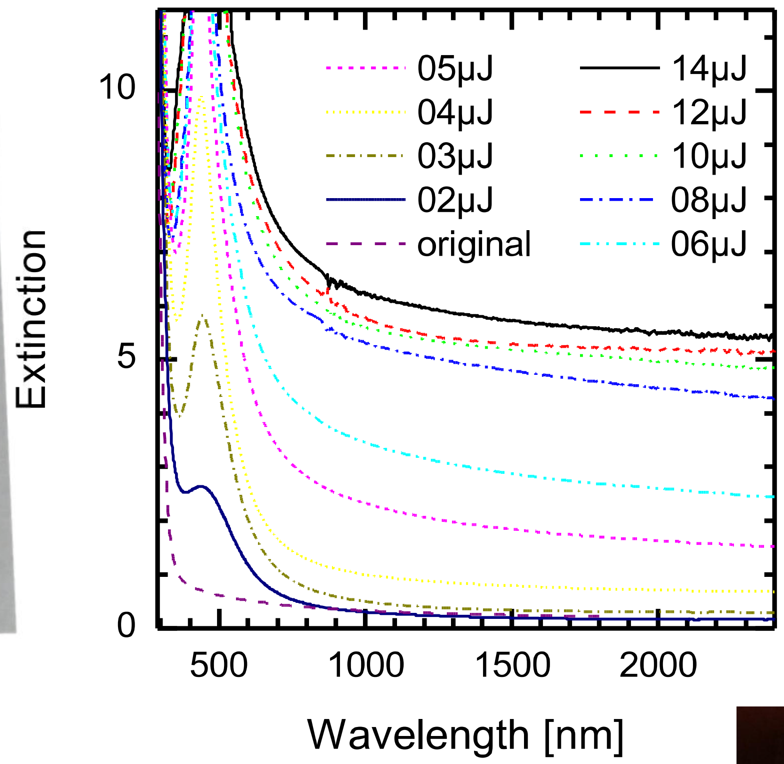




Appl. Phys. A (Rapid Commun.) **109**, 45 (2012).

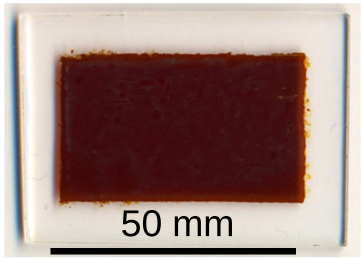
Picosecond-pulsed laser irradiation of silver-ion doped glass

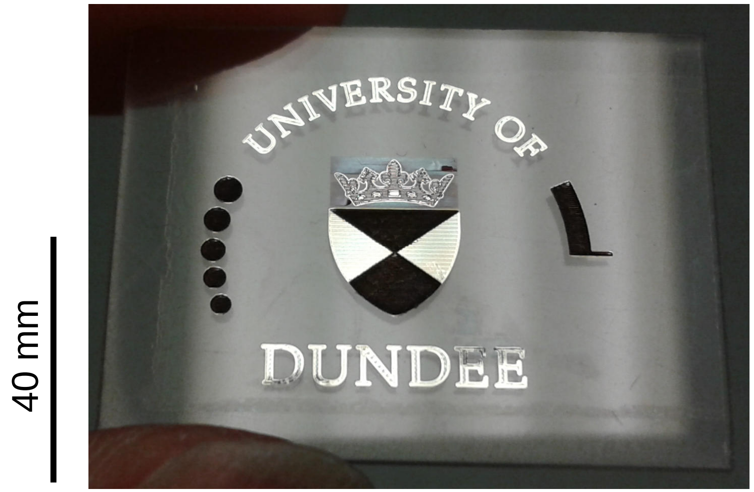


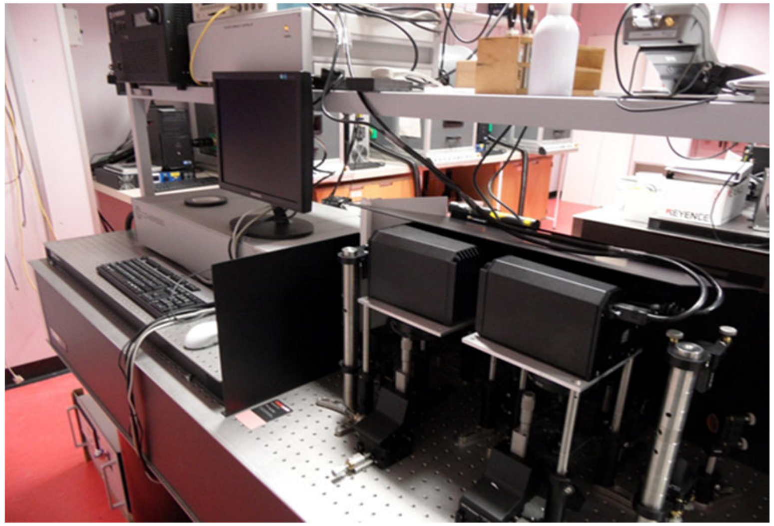


- Wavelength: **355 nm**
- Pulse length ~ **6 ps** at 80 kHz
- Beam spot diameter ~ 30 µm
- Writing speed: **20 mm/s**

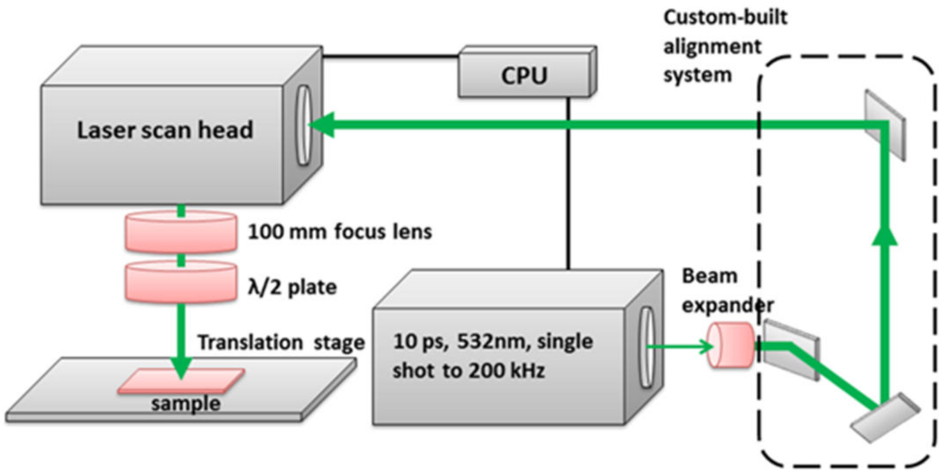
Fabricated by annealing







Coherent TALISKER laser and X-Y scanning optics

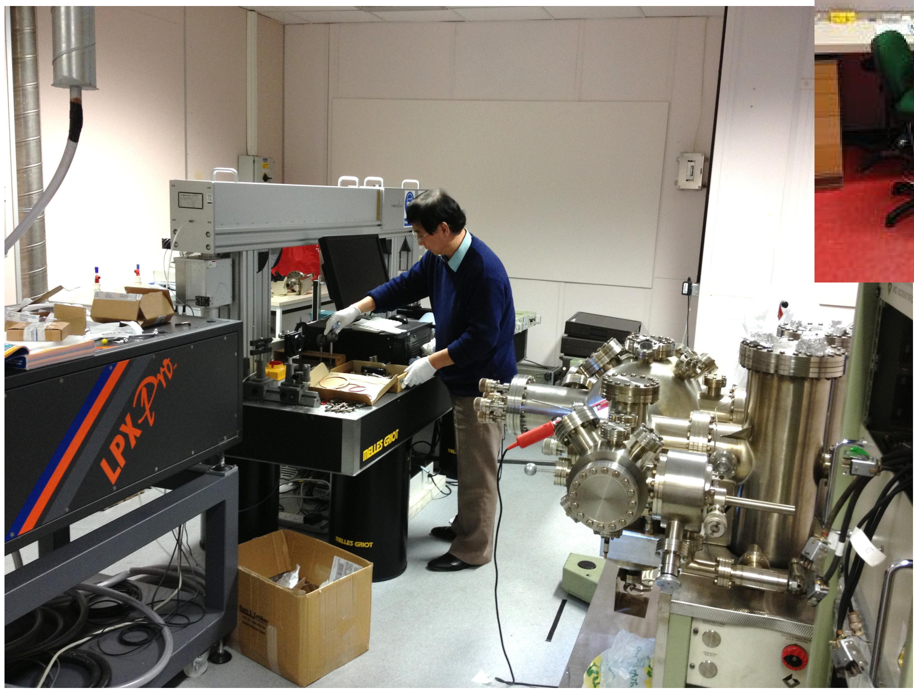


Ultrashort laser configuration for materials processing

MAPS facility contains 2 state-of-the-art laboratories for novel laser materials processing :

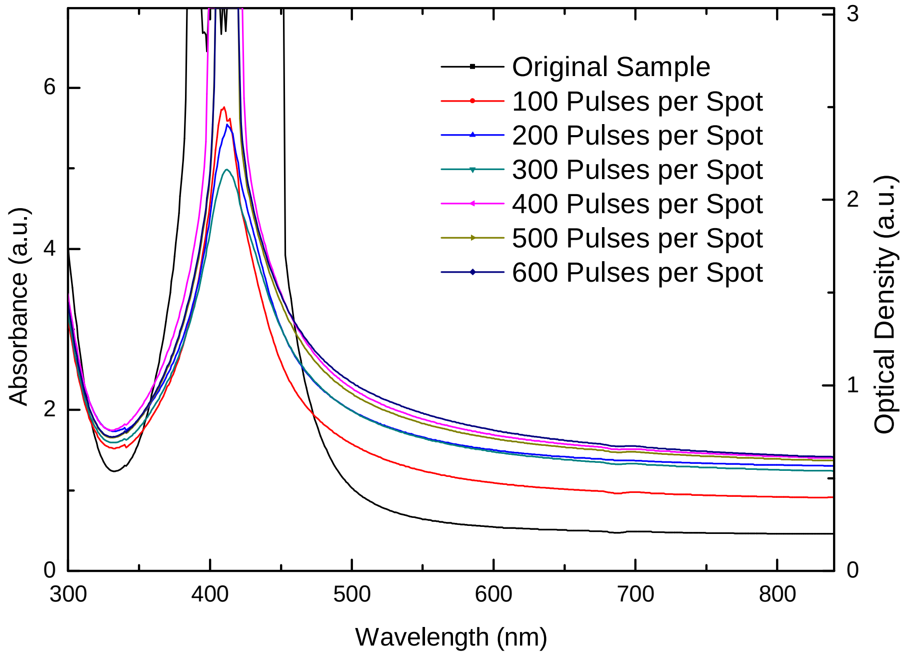
- 3 nanosecond lasers (6ns) at wavelengths 355, 532 and 1064 nm in place since 2011.
- Picosecond (Coherent Talisker ULTRA 355-04) system installed in May 2012. Operates at same 3 wavelengths, pulse width <15ps with an average power of up to 4W at 355nm, 8W at 532nm, and 16W at 1064nm.
- Coherent KrF (248nm) excimer laser system for semiconductor & materials processing
- Suite of analytical & measurement facilities, materials printer & Keyence microscopes

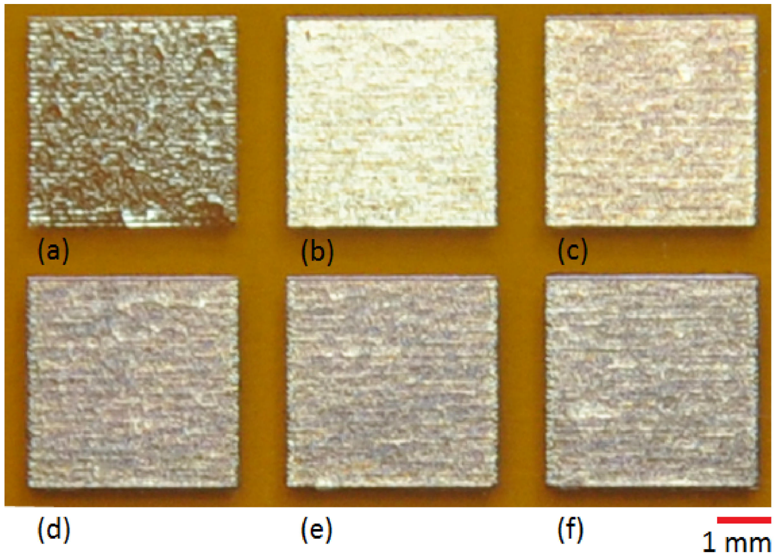
MAPS

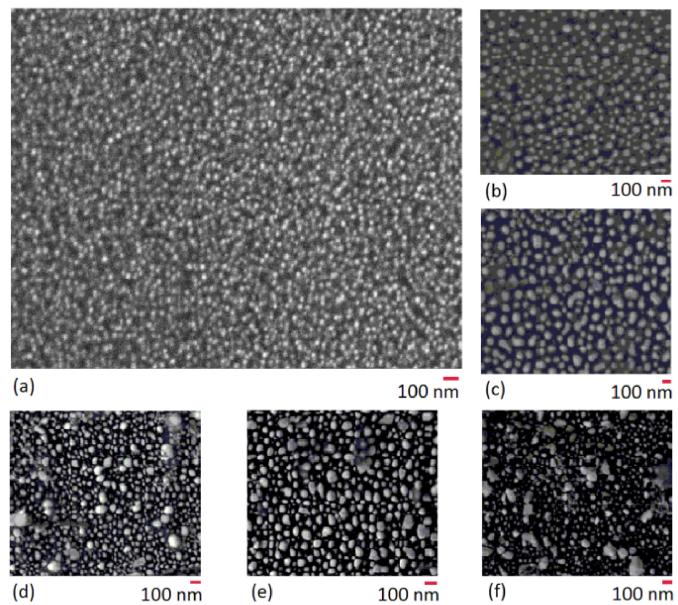


Nanosecond laser irradiation of glass with embedded silver nanoparticles at 532 nm

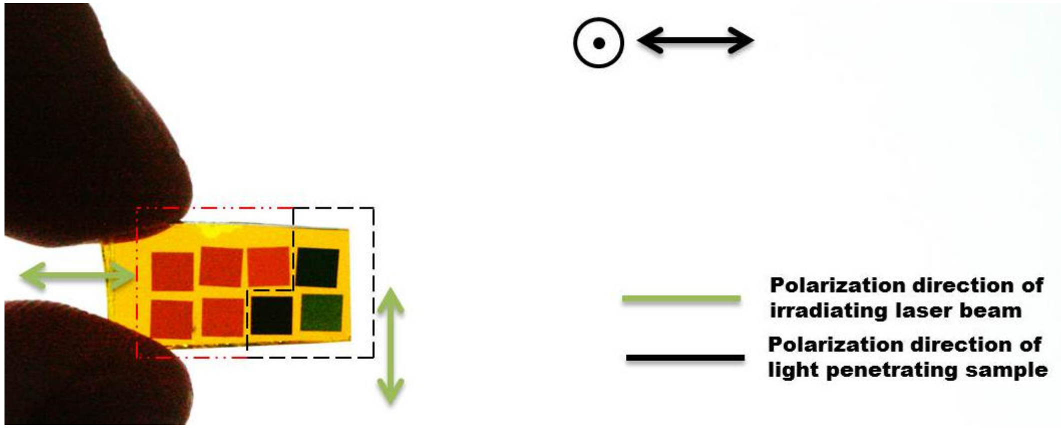
- Wavelength: **532 nm**
- Pulse length ~ **6 ns** at 50 kHz
- Laser fluence ~ 1.5 J/cm^2
- Beam spot diameter ~ 60 µm
- Writing speed: **10 mm/s**
- ~ 300 pulses per spot

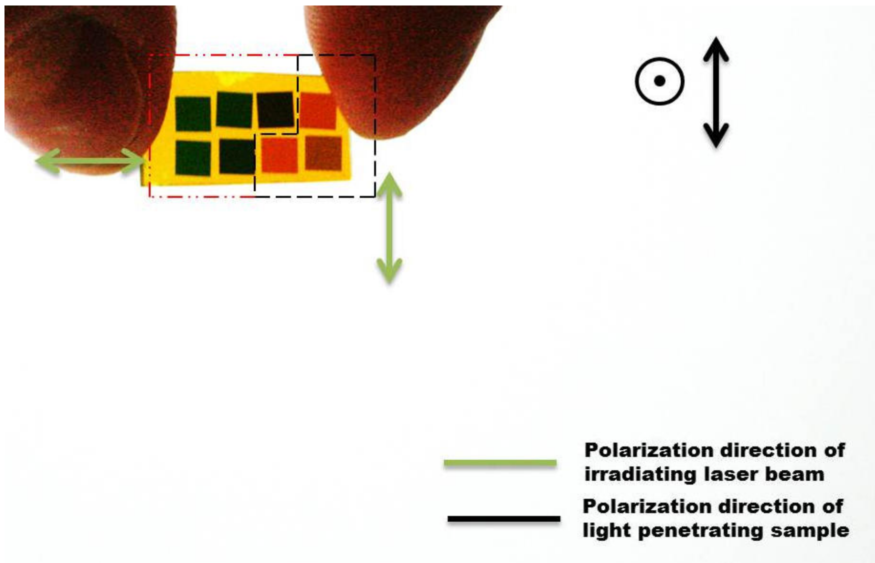






Picosecond laser irradiation of glass with embedded silver nanoparticles at 532 nm





- Wavelength: **532 nm**
- Pulse length ~ **6 ps**
- Laser fluence ≤ 0.3 J/cm^2
- Beam spot diameter ~ 15 µm
- **Top row** (left to right): 500, 300, 100, 200 pulses per spot
- **Bottom row** (left to right): 400, 200, 100,100 pulses per spot

The effects of pulse intensity and writing density on nanoparticle shape

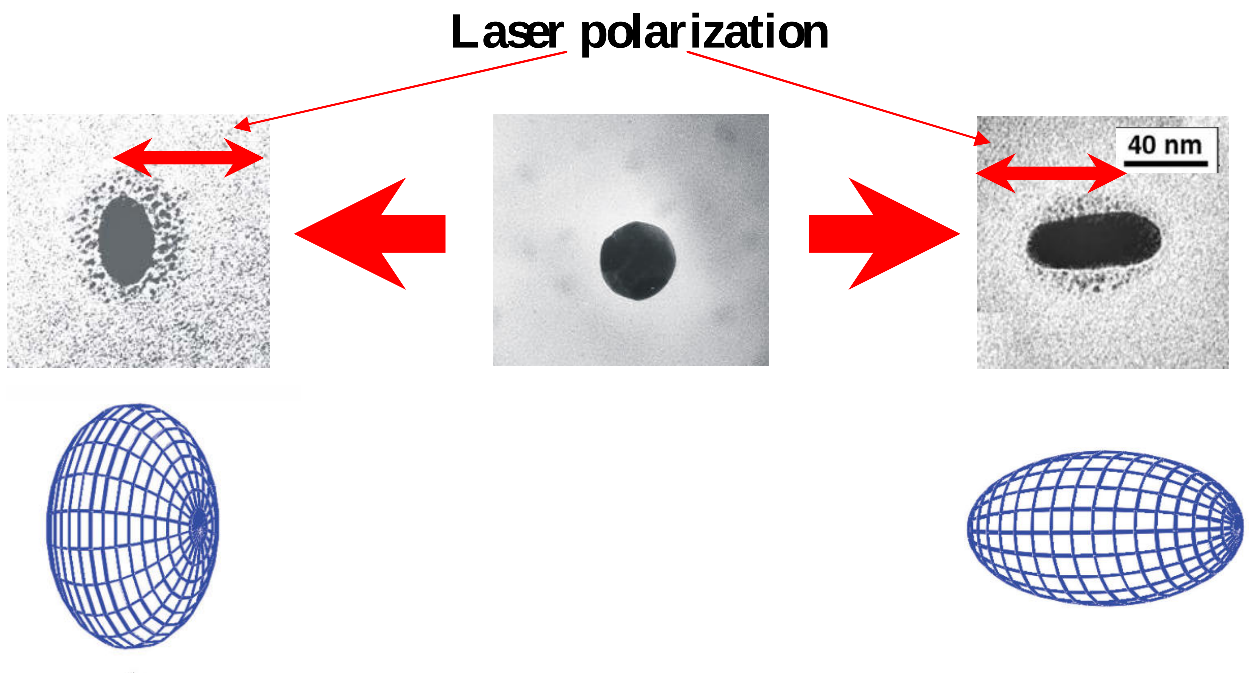
- Wavelength: 400 nm
- Pulse length ~ 150 fs,
- Linear Polarization

Single pulse irradiation
Formation of **oblate spheroids** with *short axis parallel* to laser polarization

Peak pulse intensity ~ 2.4 TW/cm^2
Energy fluence 360 mJ/cm^2

Multi pulse irradiation
Formation of **prolate spheroids** with *long axis parallel* to laser polarization

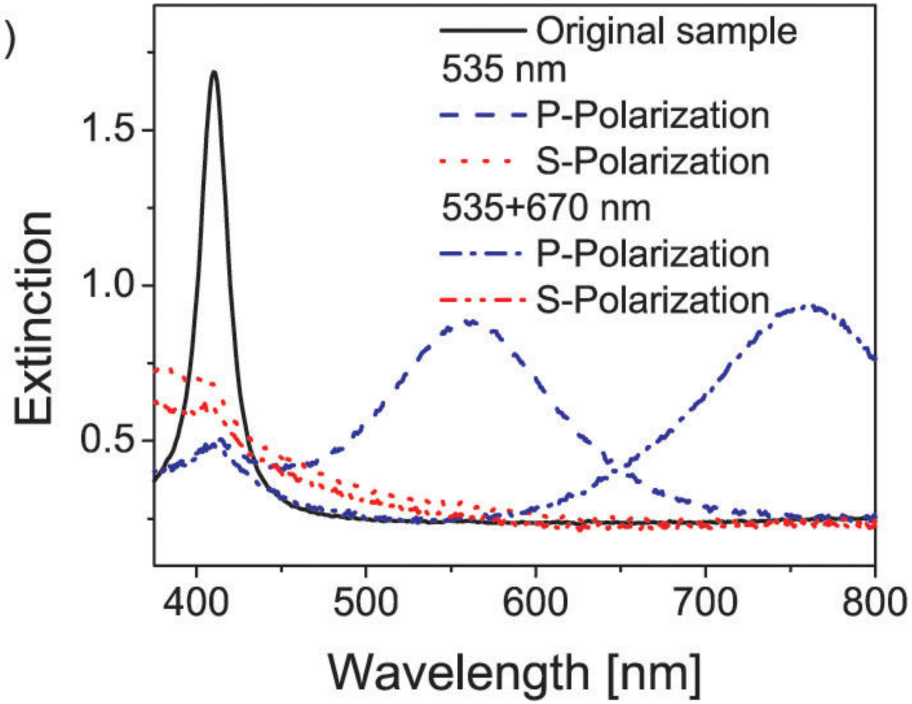
Peak pulse intensity ~ 0.4 TW/cm^2
Energy fluence 63 mJ/cm^2



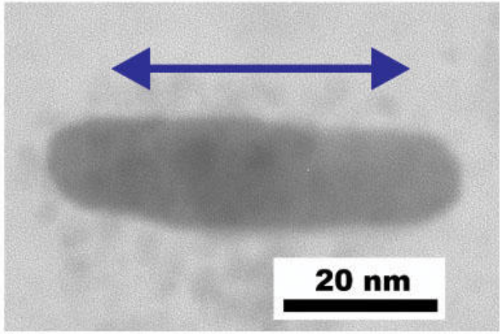
The effect of subsequent irradiation on nanoparticle shape

- 1000 pulses per spot
- Intensity ~ 1.5 TW/cm^2
- Pulse length ~ 150 fs,
- Linear Polarization

(a)



(b)

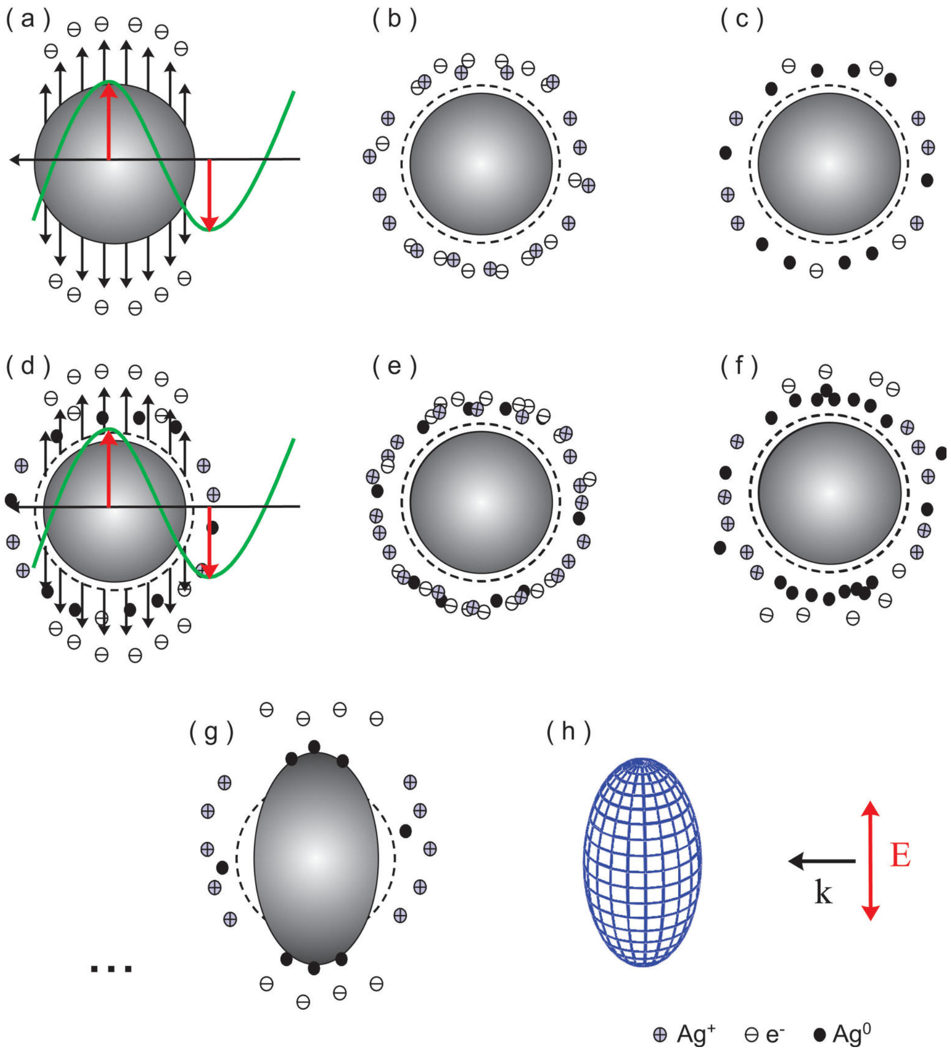


(a) Polarized extinction spectra of samples with Ag nanoparticles irradiated first with 535 nm and subsequently with 670 nm laser pulses.

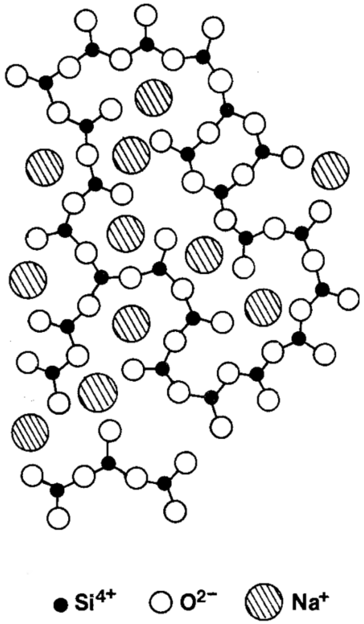
(b) TEM image of transformed nanoparticles. Laser polarization is indicated by the arrow.

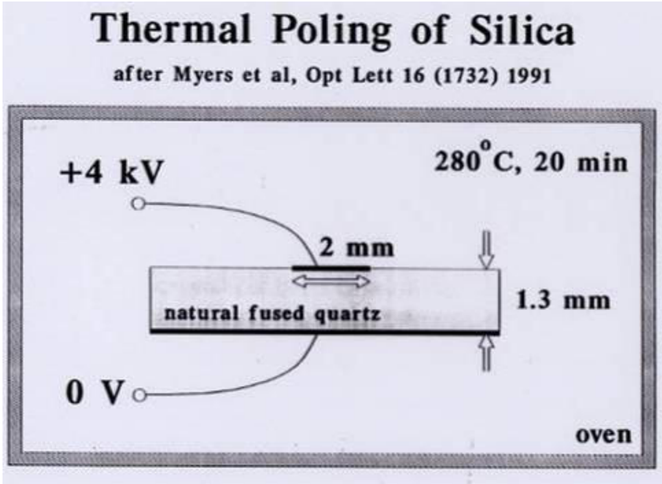
The mechanism of shape modification

Laser-assisted shape transformation metal nanospheres in the case of irradiation by linearly polarized laser pulses in low intensity (0.2-2 TW/cm^2), multi-shot mode.

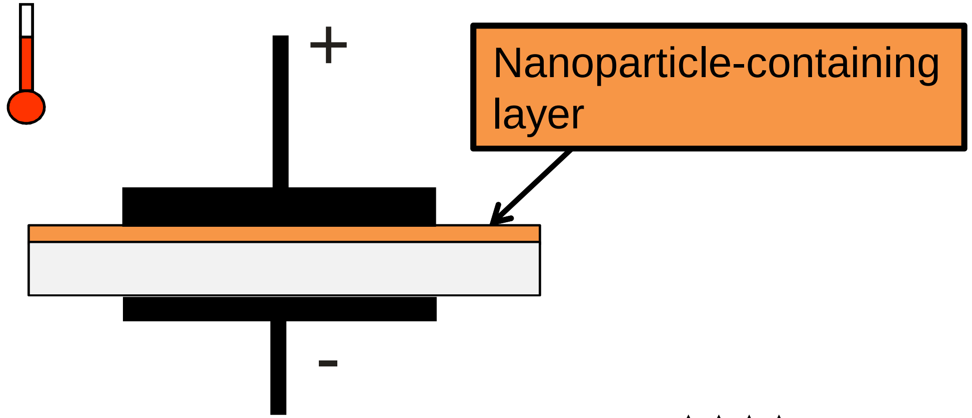


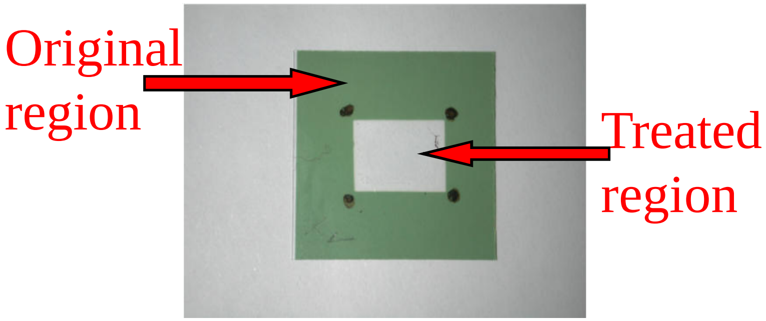
Another technique: DC electric field-assisted dissolution of nanoparticles in glass

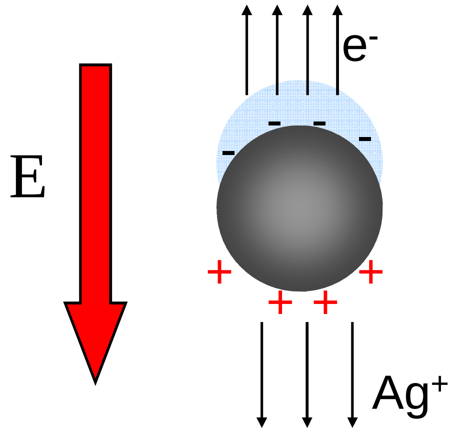


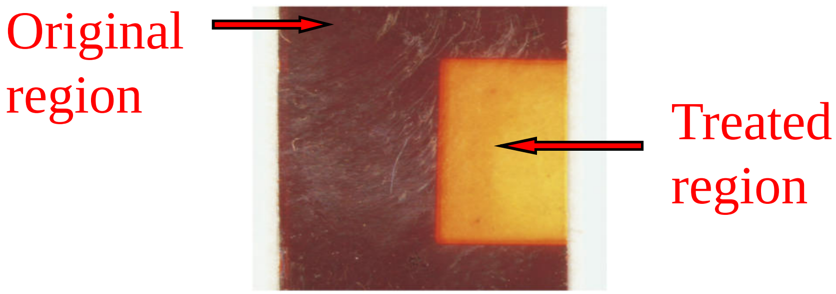

Thermal Poling of Silica

after Myers et al, Opt Lett 16 (1732) 1991



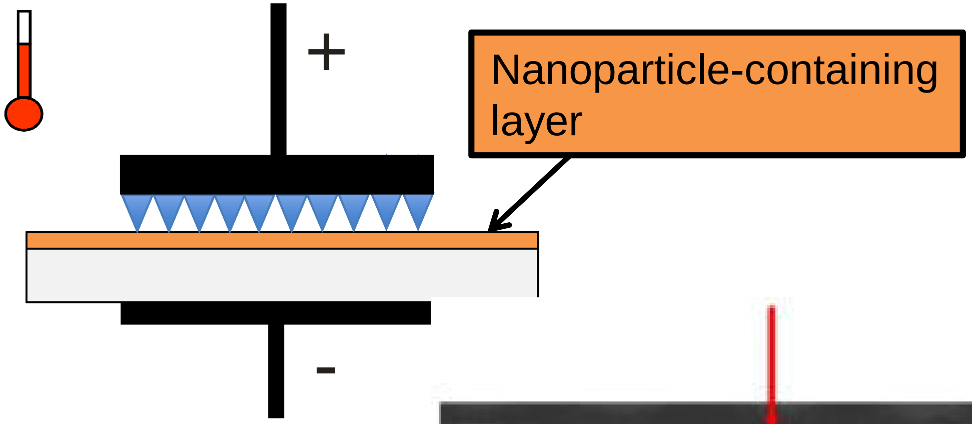


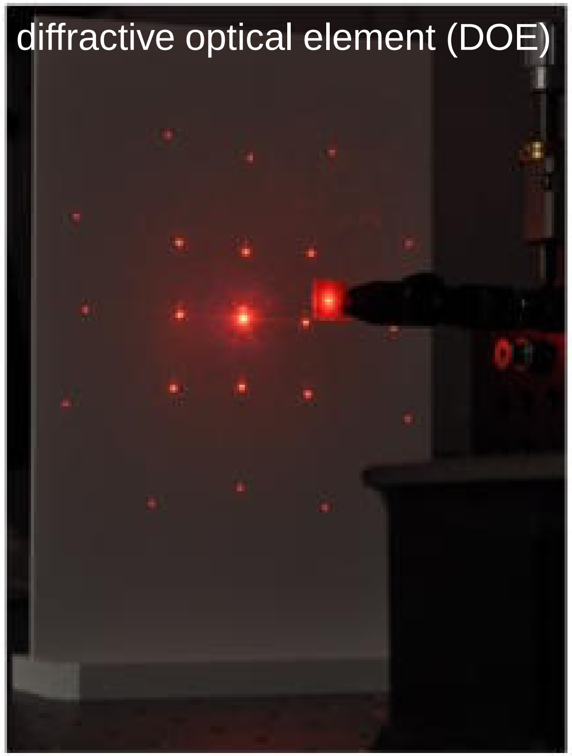


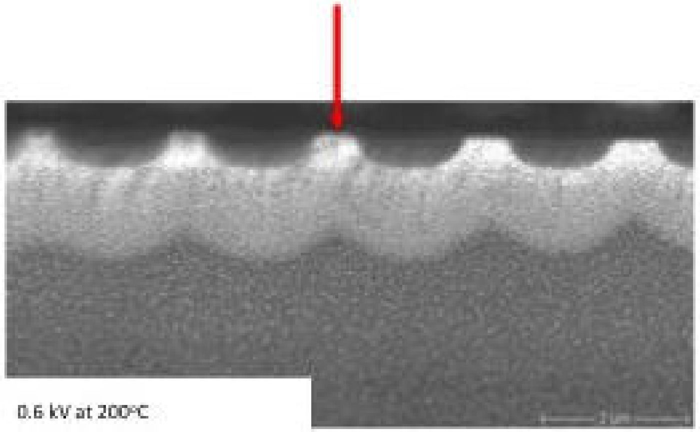


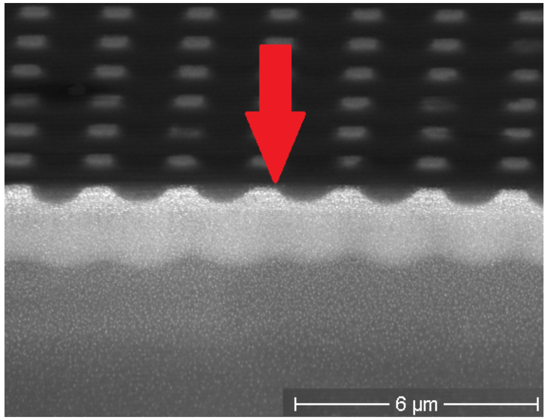
- Optics Express **20**, 22579 (2012).
- Advanced Materials **17**, 2983 (2005).
- Optics Express **13**, 1266 (2005).
- J. Phys. Chem. B **108**, 17699 (2004).
- Appl. Phys. Letters **85**, 872 (2004).

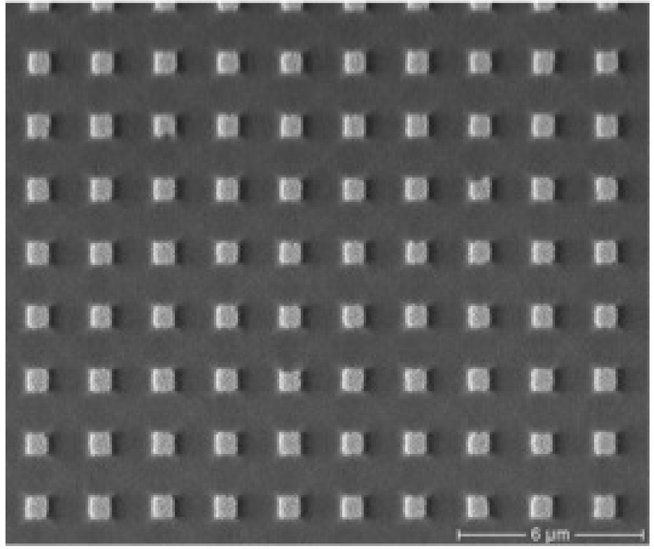
DC electric field-assisted structuring of glass with embedded metallic nanoparticles

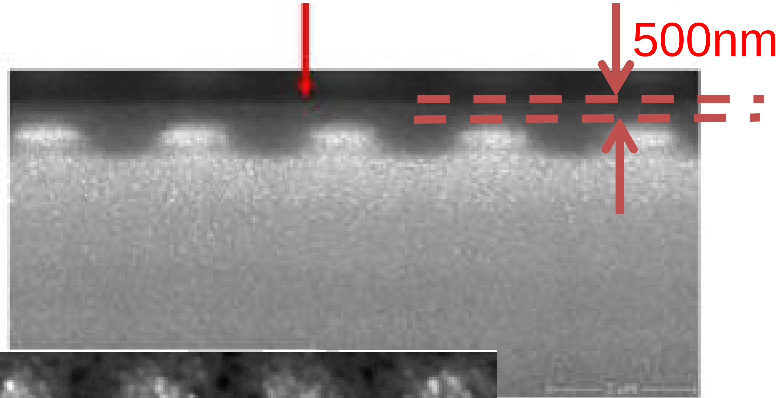


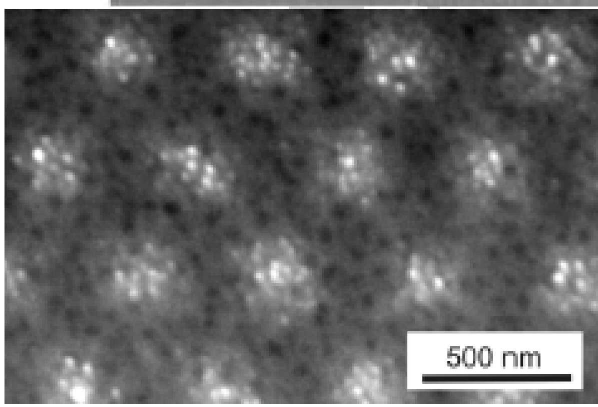












- Optics Express **20**, 22579 (2012).
- Advanced Materials **17**, 2983 (2005).

Fabrication & Engineering of Metal-Glass Nanocomposites (MGNs)

- How to fabricate tailored MGNs
- How to influence size, shape and volume filling factor of the inclusions
- How to engineer the optical properties of the MGNs

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END