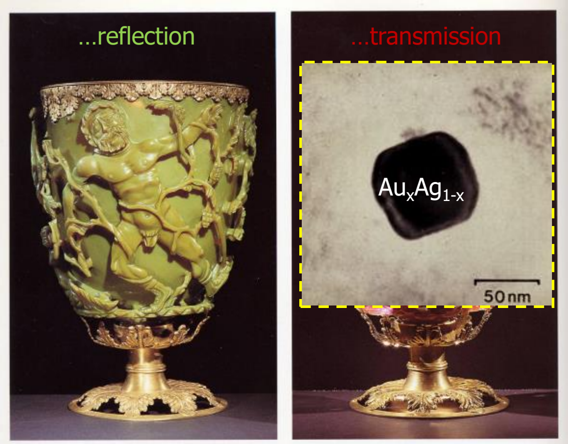
Optical Properties of Metallic Nanostructures

1. Nanotechnology: 4th Century AD



Lycurgus cup
- Roman Glass makers
- British Museum

Au_xAg_{1-x} Alloy NPs
- D ~ 70 nm,
- x ~ 0.3
- soda-lime glass

Glass	SiO_2	Na_2O	Ca_2O	MgO	Al_2O_3
Lycurgus	70	15	10	4	1
Soda-lime	73	15	7	4	1

%wt

"… It is possible to give a reddish colour to a glass by adding a small amount of gold powder …"

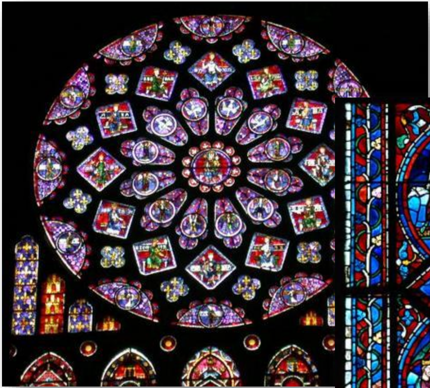
(J. Kunckel, German Chemist, 17th century)

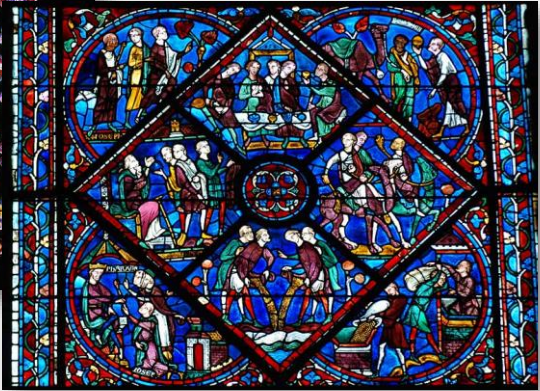
Plasmonic Art: 1248

La Sainte-Chapelle
(Paris, France, 1248)

Stained Glasses

Plasmonic Art: 1250

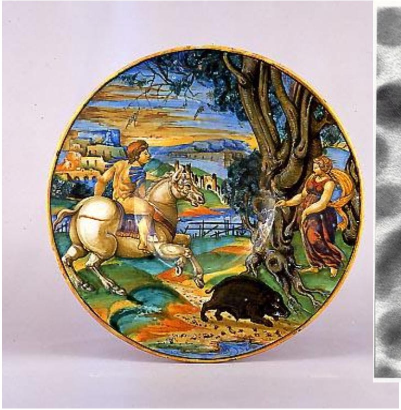


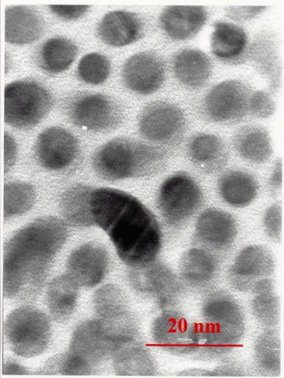


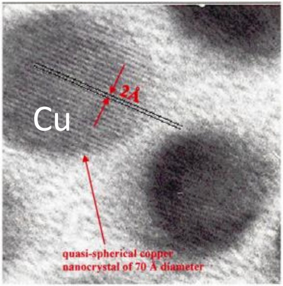
Chartres Cathedral
(Chartres, France, 1250)

Stained Glasses

2. Nanotechnology 16th century







Cu or Ag NPs
D ~ 5-10 nm

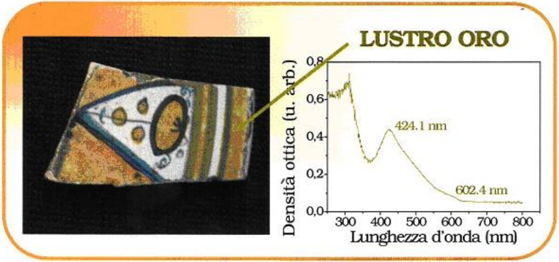
Lustres in Gubbio and Deruta (Italy)

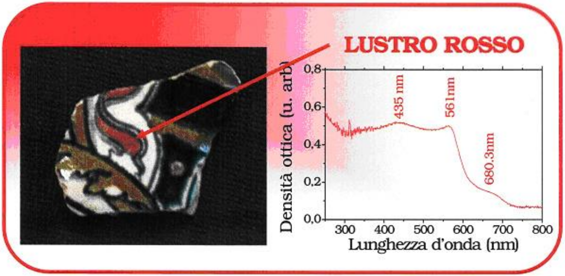
- Lustre Dish with Pico, Circe and Canente legend.
- Lustred by Mastro Giorgio
- Museum of Pottery, Gubbio, Italy, 1528

Recipe for the Lustre (Gubbio, 16th century)

- deposition of Ag or Cu salts or oxides in solution with vinegar
- thermal heating at 600 °C in a standard furnace with dry broom

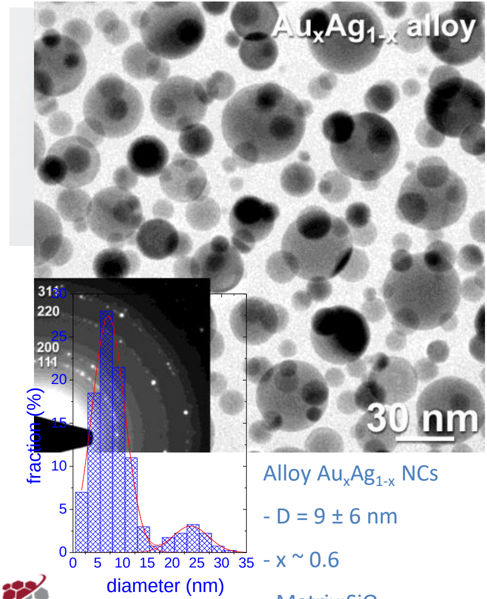
2. Nanotechnology 16th century





The lustre's color is linked to its optical absorption

3. Nanotechnology: 21st century



Alloy Au_xAg_{1-x} NCs

- D = 9 ± 6 nm

- x ~ 0.6

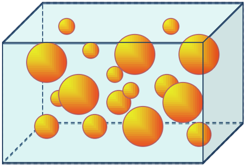
- Matrix:SiO_2

Ion Implantation in SiO_2

- Au, 190 keV, 3e16 ions/cm^2
- Ag, 90 keV, 3e16 ions/cm^2
- Thermal annealing (air, 800°C, 1 hour)

Ion implantation

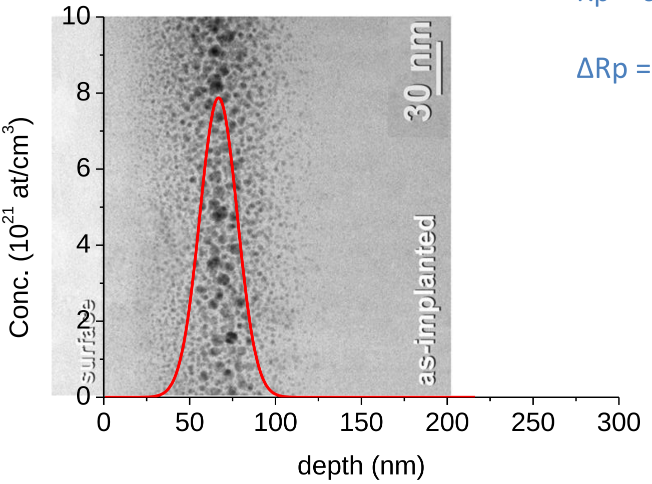
Ion Implantation



Dielectric Matrix (glass)

Metal NanoParticles (NPs)

Example: Au 190 keV, 3×10^{16} ion/cm^2 in SiO_2



Rp = 67 nm

ΔRp = 11 nm

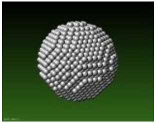
Sequential Ion Implantation

Size

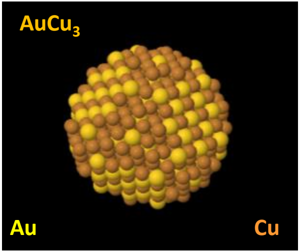
Composition

Structure

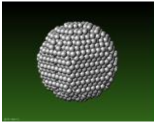
D ~ 1 nm

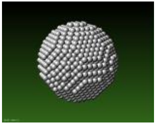


D ~ 4 nm



Co hcp

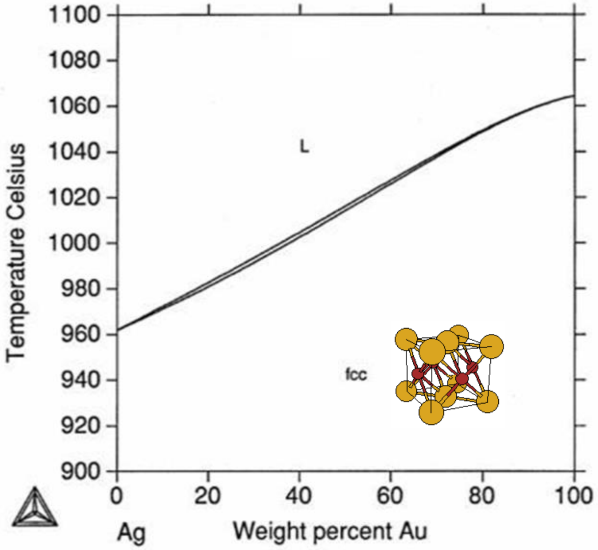




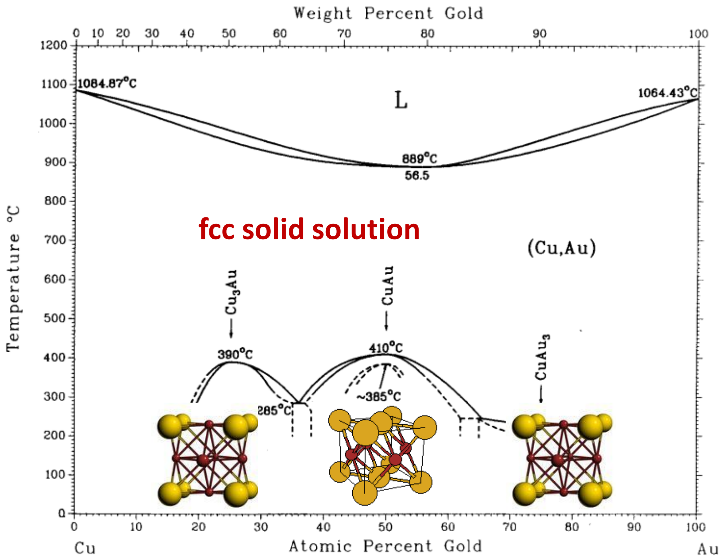
Co fcc

Innovative functionalities from composition control

Bulk Au-Ag binary phase diagram



Bulk Au-Cu binary phase diagram



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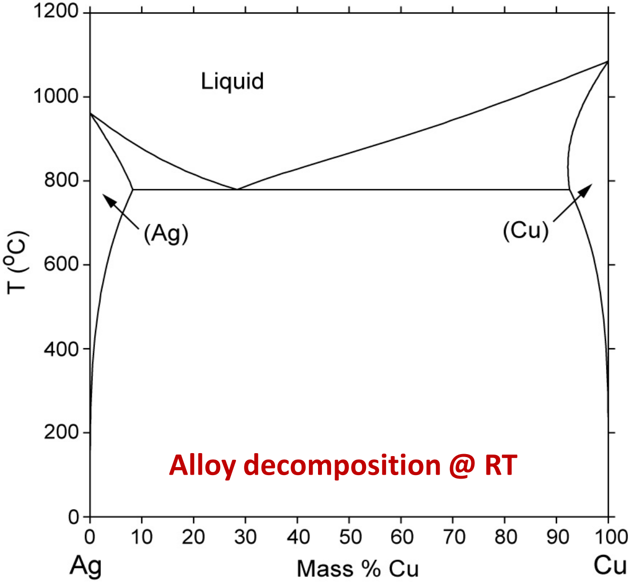
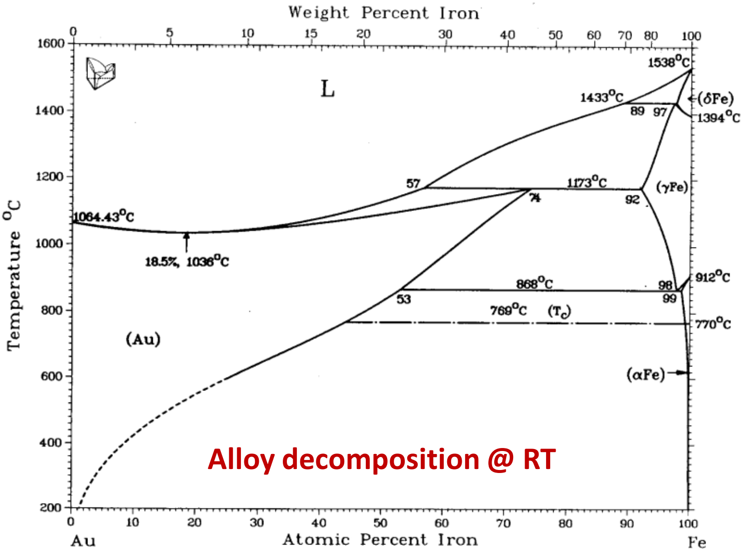


Bulk Au-Fe binary phase diagram

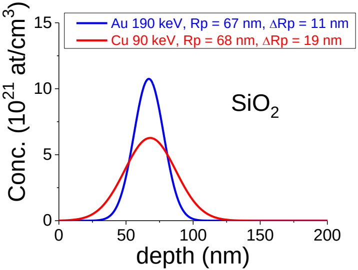


Alloy decomposition @ RT

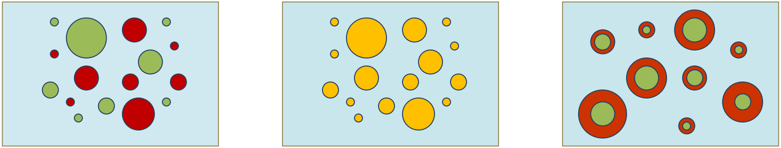
Impianto Ionico

Sequential Ion Implantation

(es.: Au + Cu, 3×10^{16} ion/cm^2 in SiO_2)



Three different clusters morphologies can be expected after sequentially implanting elements A and B



A and B separated

A-B alloy

A core B shell

Ion Implantation

- Implantation **Energy** and **Fluence** to maximize overlapping (multiple-energy implants for flattening the concentration profiles)
- **Miscibility** of the implanted elements (ΔH_{mix}) – nano-alloying
- **Chemical interaction** with the matrix
- **Radiation-induced defects** (radiation enhanced diffusion)

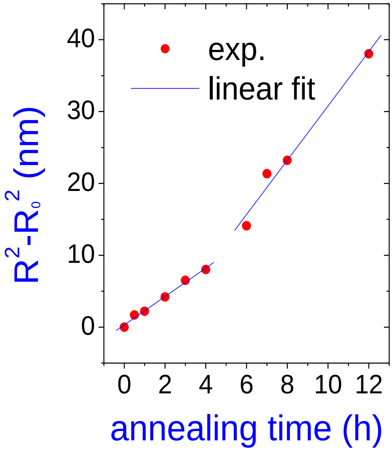
Post-Implantation Annealings or Irradiation

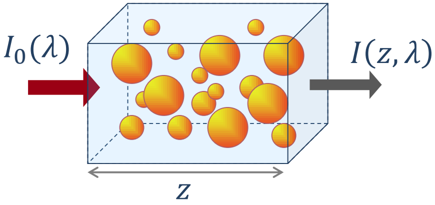
- **Preferential interaction** of one element with the annealing atmosphere or vacancy creation via ion-irradiation
- **Annealing** of the radiation-induced defects

Linear Optical Properties

Au NPs in SiO_2

Au 190 keV, 3×10^{16} ions/cm^2 in SiO_2





$$I(z,\lambda) = I_0(\lambda)e^{-\gamma(\lambda)z}$$

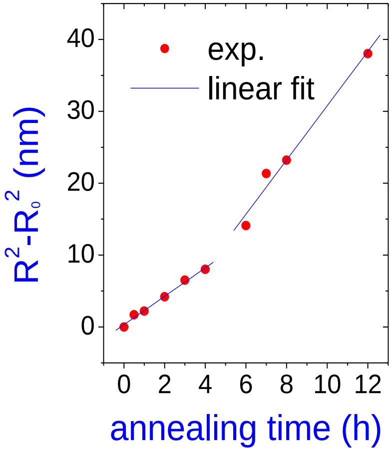
$$T(\lambda) \equiv \frac{I(z,\lambda)}{I_0(\lambda)} = e^{-\gamma(\lambda)z}$$

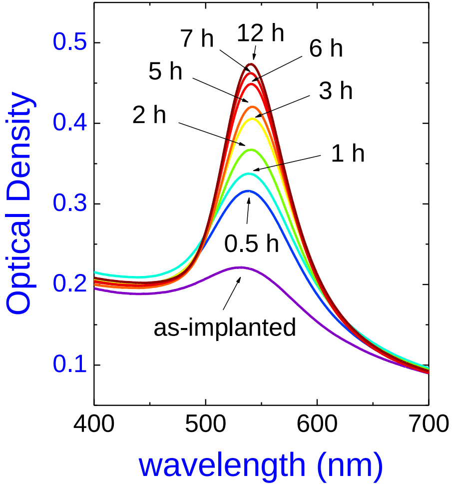
$$A(\lambda) \equiv log_{10}\frac{1}{T(\lambda)} = -log_{10}T(\lambda)$$

Absorption measurements in the VIS-NIR spectral range

Linear Optical Properties

Au 190 keV, 3×10^{16} ions/cm^2 in SiO_2



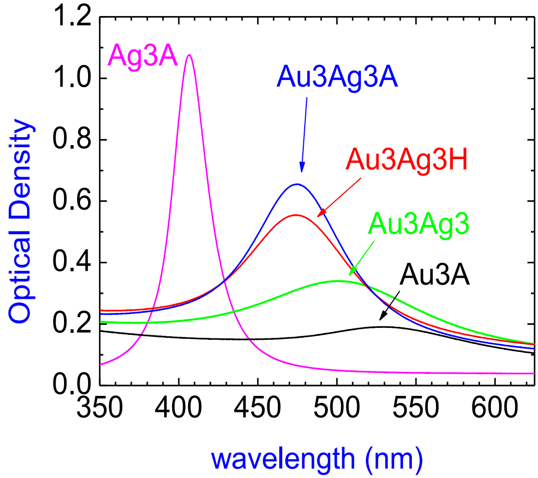


Optical Absorption Band around 535 nm (Surface Plasmon Resonance – SPR)

Linear Optical Properties

Au-Ag alloy NPs in SiO_2

Au-Ag nanoalloy Optical Properties



Au3Ag3 as-implanted — **SPR: 501 nm**

Au3Ag3H 800 °C, 1h, H_2-Ar — **SPR: 475 nm**

Au3Ag3A 800 °C, 1h, air — **SPR: 475 nm**

Au3A 800 °C, 1h, air — **SPR: 530 nm**

Ag3A 800 °C, 1h, air — **SPR: 407 nm**

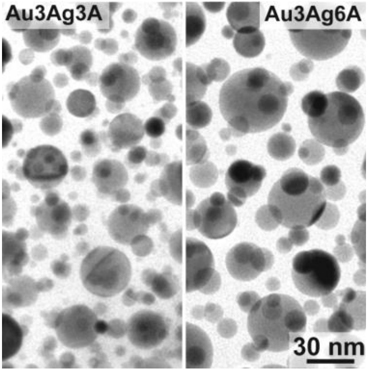
Vegard's Law for the lattice paramenterof an alloy $A_x B_{1-x}$

$$a_{AB} = x a_A + (1-x) a_B$$

SPR band of the Au-Ag alloy is between that of the pure Au and Ag (like for Vegard's law)

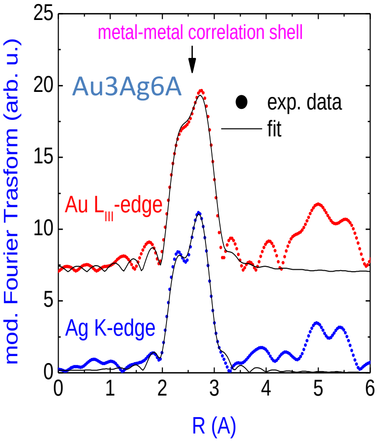
Au-Ag nanoalloy Optical Properties

TEM



Au3Ag3A	Au3Ag6A
3×10^{16} Au^{+}/cm^{2}	3×10^{16} Au^{+}/cm^{2}
3×10^{16} Ag^{+}/cm^{2}	6×10^{16} Ag^{+}/cm^{2}
800C 1h air	800C 1h air
<D>=9.1 ± 5.8 nm	<D>= 14.3 ± 7.9 nm

EXAFS analysis at Ag K-edge and Au L_{III}-edge



AuAg alloy