The optical properties of metal nanoparticles (NPs) are determined by a collective oscillation of the free electrons in the particles which is mostly described by the term plasmon resonance absorption. The oscillation frequency is determined by the main factors: the electronic density, the effective electronic mass, the shape, size and distribution of the particles in the polymer matrix. Poly(vinyl alcohol) (PVA) is a polymer highly transparent in the visible spectral domain, and due to its solubility in water, the silver NPs can be easily prepared from aqueous media.

### II. Plasmon resonance

When a nanoparticle is much smaller than the wavelength of light, coherent oscillation of the conduction band electrons induced by interaction with an electromagnetic field. This resonance is called localized plasmon resonance.

### III. Metal nanoparticles

<table>
<thead>
<tr>
<th>Metal species</th>
<th>E0 (V)</th>
<th>Reducing agent</th>
<th>Conditions</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au3+</td>
<td>&gt; 0.7</td>
<td>Alcohols, polyols, Aldehydes, sugars, Hydrazine, H3PO2, NaBH4, boranes, Citrate</td>
<td>&gt; 70°C</td>
<td>Slow</td>
</tr>
<tr>
<td>Cu2+</td>
<td>&lt; 0.7</td>
<td>Polyols, Aldehydes, sugars, Hydrazine, hydrogen</td>
<td>&gt; 120°C</td>
<td>Slow</td>
</tr>
</tbody>
</table>

Experimental techniques to synthesize metal nanoparticles: laser ablation, photochemical reduction, heat evaporation (including chemical vapor deposition) and chemical reduction.

In general, the chemical reduction reactions involve reducing agents that are reacted with a salt of the metal according to the following chemical equation:

\[ \text{nMe}^{2+} + \text{nRe} \rightarrow \text{nMe}^{0} + \text{nRe}\]

Ag-PVA nanocomposite films prepared from AgNO3 and an aqueous solution of PVA (8% w/w, MW = 85000-240000, hydrolisis: 87-89%).

Film preparation:
- Spin coating (6000 rpm – 15 s) on piranha-cleaned silicon wafers
- Dry film thickness: 1 – 2 µm
- Final silver concentration: 8.4%

### IV. In situ synthesis of metal nanoparticles

Film annealing:
- 10 to 60 minutes at 90°C.

By increasing the annealing time and temperature, the coatings became yellowish-brown in color.

Reference films: same without silver salt.

### V. Structural properties

Surface morphology of the films was studied by AFM in tapping mode.

AFM images of pure PVA film (scale bar: 200 nm)
- (A) topography; (B) phase

AFM topographic images of Ag-PVA films (scale bar: 200 nm)
- (A) Non-annealed film
- (B) Film annealed 10 min @ 90°C
- (C) Film annealed 60 min @ 90°C

### VI. Optical properties by spectroscopic ellipsometry

Optical model: one layer (Cauchy) and Lorentzian absorption

Optical properties studied by spectroscopic ellipsometry (SE)

\[ \rho = \frac{\rho_1}{\rho_1} = \tan \Psi e^{i\Delta} \]

Optical properties of the AG-PVA films annealed at 90°C during 10, 30, 45 and 60 min (from bottom curve to top curve).

In situ synthesis of silver NPs embedded in PVA films.

Formation of NPs was evidenced by AFM: a strong material contrast between the NPs and the matrix, reflecting the different atomic composition of both film components.

Optical properties by spectroscopic: very intense and localized absorption band at 420 nm.

Intensity of the plasmon band was highly correlated to the density of NPs.

Method also applied to gold and platinum NPs.

Complex mechanism of NPs formation in films with respect to solutions.

Applications to plasmon-enhanced absorption devices.

### Conclusion and further work

- In situ synthesis of silver NPs embedded in PVA films.
- Formation of NPs was evidenced by AFM: a strong material contrast between the NPs and the matrix, reflecting the different atomic composition of both film components.
- Optical properties by spectroscopic: very intense and localized absorption band at 420 nm.

- Intensity of the plasmon band was highly correlated to the density of NPs.
- Method also applied to gold and platinum NPs.
- Complex mechanism of NPs formation in films with respect to solutions.
- Applications to plasmon-enhanced absorption devices.