Optical Properties of Metal Nanoparticles Embedded in a Polymer Matrix

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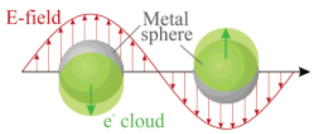
I. Introduction

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 of **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

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 :

$$mMe^{n+} + n\,Red \rightarrow mMe^{0} + nOx$$

Metal species	E0 (V)	Reducing agent	Conditions	Rate
Au^{3+} Ag^{+}	≥ + 0.7	Alcohols, polyols Aldehydes, sugars Hydrazine, H3PO2 NaBH4, boranes Citrate	≥ 70°C < 50°C Ambient Ambient > 70°C	Slow Moderate Fast Very fast Moderate
Cu^{2+}	< 0.7 And ≥ 0	Polyols Aldehydes, sugars Hydrazine, hydrogen NaBH4	> 120°C 70-100 °C < 70°C Ambient	Slow Slow Moderate Fast

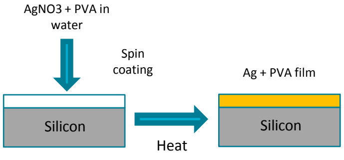
Table 1 : **Reagents most commonly used in the reduction of gold, silver, and copper salts** along with the appropriate conditions.

IV. *In situ* synthesis of metal nanoparticles

Ag-PVA nanocomposite films prepared from AgNO3 and an aqueous solution of PVA (8% w:w , MW = 85000-24000, hydrolysis: 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%



Film annealing :

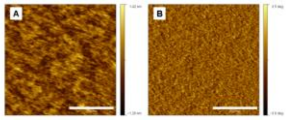
- 10 to 60 minutes at 90°C.

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

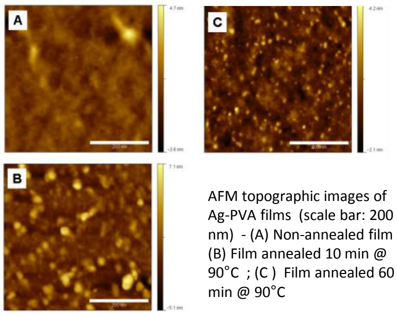
Reference films : same without silver salt

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)

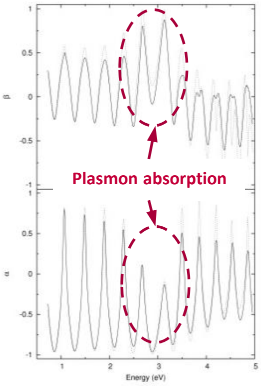


AFM topographic images of Ag-PVA films (scale bar: 200 nm) - (A) Non-annealed film ; (B) Film annealed 10 min @ 90°C ; (C) Film annealed 60 min @ 90°C

VI. Optical properties by spectroscopic ellipsometry

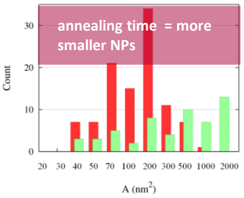
Optical properties studied by **spectroscopic ellipsometry** (SE)

$$\rho = \frac{|r_p|}{|r_s|} = \tan\,\Psi\, e^{i\Delta}$$

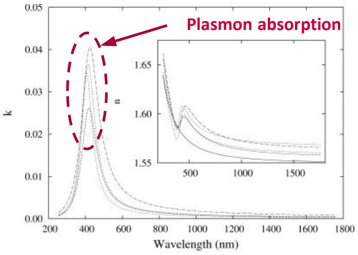


Optical model : one layer (Cauchy) and Lorentzian absorption

PVA film annealed 10 min at 90°C (SE data and regression results)



Statistical distribution of the particles area (green: annealing time = 10 min; red: annealing time = 60 min).



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

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

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