Realtime spectroscopic ellipsometry of plasmonic Nanoparticles growth in PolyVinyl Alcohol thin films

Patrick KFOURY(a)*, Yann BATTIE(a), Aotmane EN NACIRI(a), Laurent BROCH(a), Michel VOUE(b), and Nouari CHAOUI(a)

a : LCP-A2MC, Université de Lorraine, ICPM, 1 Bd Arago 57070 Metz, France

b : LPMO, Université de Mons, Institut de Recherche en Science et Ingénierie des Matériaux, Place du Parc, 20, 7000 Mons, Belgique

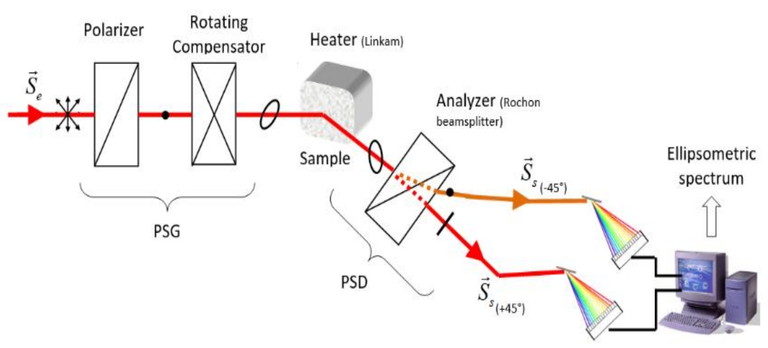
* Patrick.Kfoury@univ-lorraine.fr

Context

- Silver nanoparticles thermal growth in PVA thin films.
- Realtime monitoring by spectroscopic ellipsometry in the visible spectral range.
- Ellipsometric spectra analysis with the Shape Distributed Effective Medium Theory.
- Films' optical properties determination.
- Growth kinetics interpreted from volume fraction time evolution.

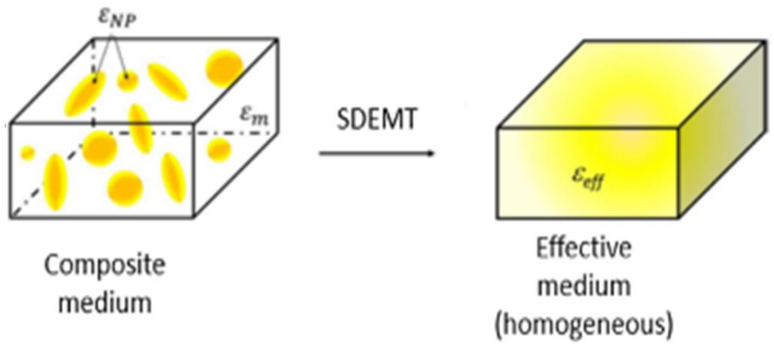
Materials and methods

- Spin-coating at 5000 rpm of AgNO3-PVA aqueous solutions.
- Realtime Rotating Compensator Spectroscopic Ellipsometry.
- Transmission Electron Microscopy



Model

Shape Distributed Effective Medium Theory



$$\varepsilon_{eff} = \frac{(1-f)\varepsilon_m + f\varepsilon_{NP} < \beta >}{(1-f) + f < \beta >}$$

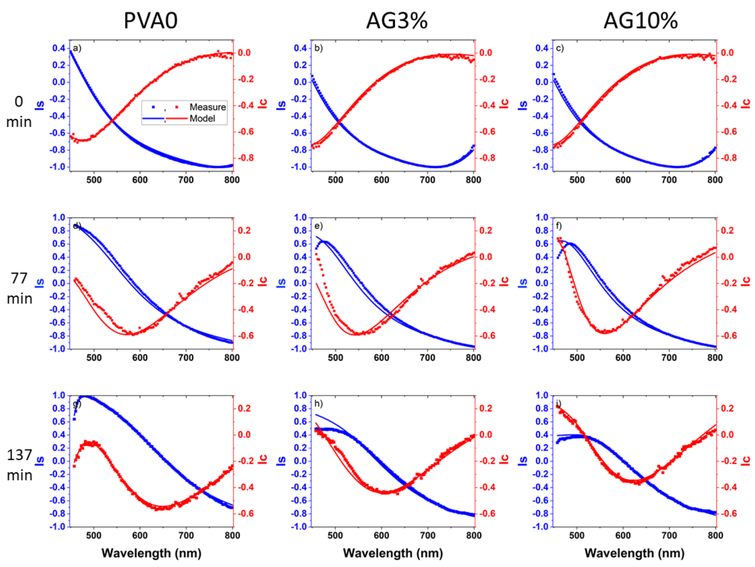
$$\beta(L_1, L_2) = \frac{1}{3}\sum_{i=1}^{3} \frac{\varepsilon_m}{\varepsilon_m + L_i(\varepsilon_{NP} - \varepsilon_m)}$$

$$L_i = \frac{r_2 r_3}{2}\int_0^{+\infty} \frac{dq}{(q + r_i^2)\sqrt{\prod_{i=1}^{3}(q + r_i^2)}}$$

SDEMT takes into account the shape distribution of NPs inside the dielectric matrix and the depolarization parameters are related to the three aspect ratios of the NPs considered ellipsoids with three main axes.

Results

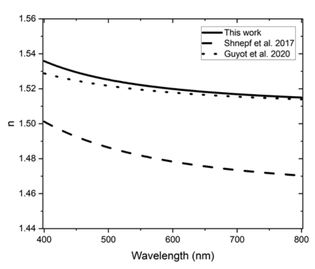
Ellipsometric spectra



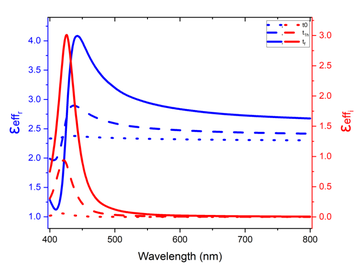
≠ Spectra → ≠ Optical pr.
Model ~ Measure

Optical Properties

PVA0 n, k=0

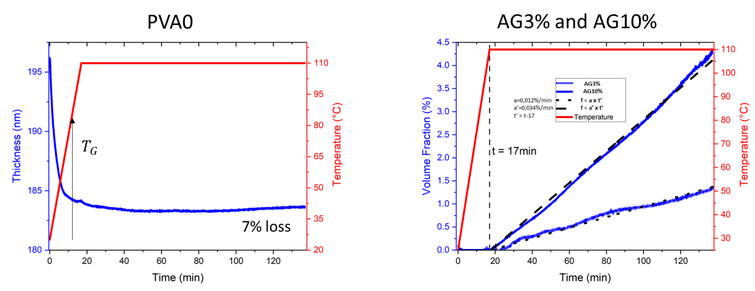


AG10%



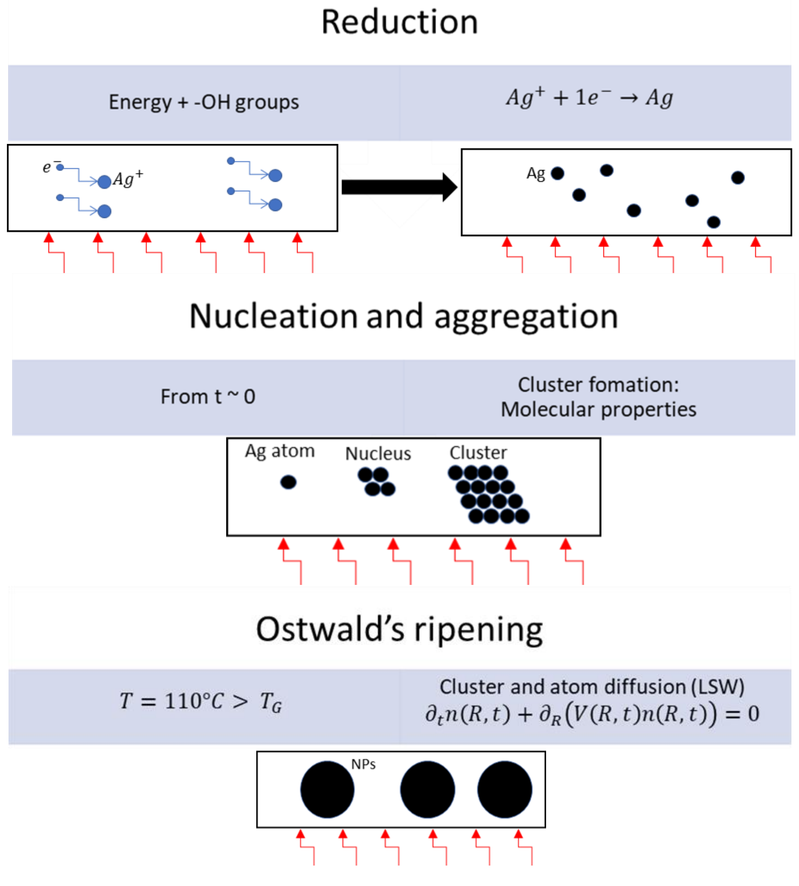
- Evolution of the dielectric function: Kramers-Kronig equations ✓
- $422\text{nm} < \lambda_{res} < 426\text{nm}$: Fröhlich's condition – Spherical AgNPs

Thickness and volume fraction time evolution



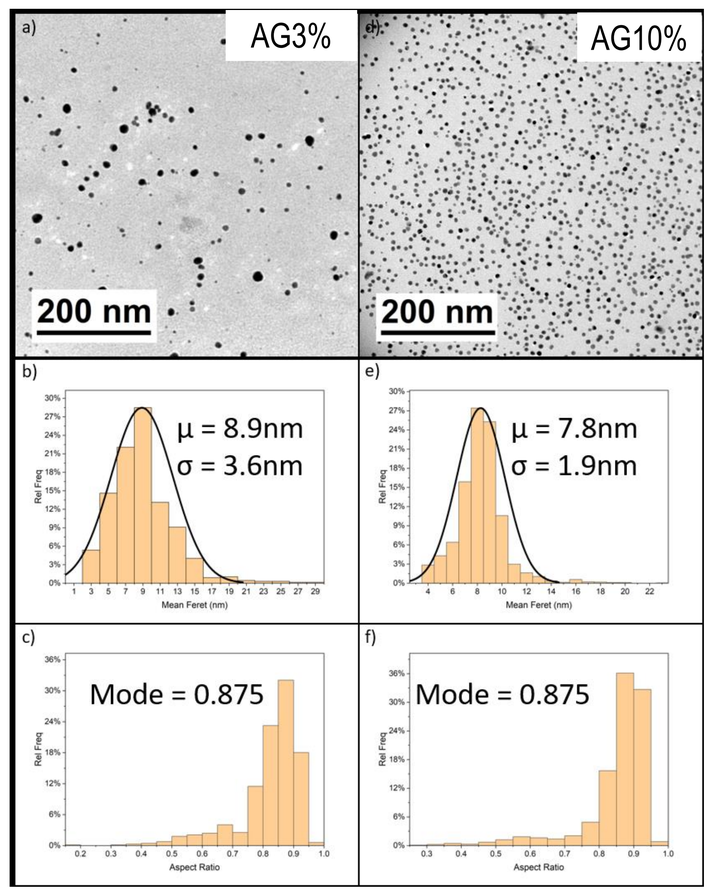
- Film shrinking during annealing due to excessive solvent evaporation
- Growth detection begins at 17 min
- Slow Zero order kinetic time evolution of volume fraction → Diffusion limited

Growth mechanism



Results

TEM imaging



Aspect ratio distribution based on SE results and SDEMT calculations

Spherical centered distributions

Conclusion

- Silver NPs growth in PVA matrix by thermal annealing
- Optical in situ monitoring by SE
- SDEMT modeling:
  - ➢ Thickness: loss during annealing
  - ➢ Volume fraction time evolution: Zero order kinetic
  - ➢ Growth mechanism: governed by Ostwald's ripening
  - ➢ Shape distribution: Spherical centered

References

- S. Porel et al., Chem. Mater. 17(1), 9–12 (2005).
- T.W.H. Oates, Appl. Phys. Lett. 88(21), 213115 (2006).
- M. Voué et al., Thin Solid Films 519(9), 2963–2967 (2011).
- A. Resano-Garcia et al., The Journal of Chemical Physics 142(13), 134108 (2015).
- L. Broch et al., Thin Solid Films 571, 509–512 (2014).
- M.J. Schnepf et al., Nanoscale 9(27), 9376–9385 (2017).
- C. Guyot et al., Journal of Vacuum Science & Technology B 38(1), 013602 (2020).
- I.M. Lifshitz, and V.V. Slyozov, Journal of Physics and Chemistry of Solids 19(1–2), 35–50 (1961).
- C. Wagner, Berichte Der Bunsengesellschaft Für Physikalische Chemie 65(7–8), 581–591 (1961).
- C.W. Price, Acta Metallurgica et Materialia 38(5), 727–738 (1990).