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Plasmonic nanoparticles growth in polymeric thin films in situ monitored by spectroscopic ellipsometry

F. Smart materials for nanoelectronics and nanophotonics

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Abstract

The growth of metallic nanoparticles has been the subject of interest for many studies due to their physical properties and vast fields of applications. In particular, these NPs exhibit remarkable optical properties with plasmonic resonance bands depending on their size, their shape and their host medium.

The growth of metallic NPs in polymeric films gives rise to nanocomposite materials with interesting optical properties and applications such as non-linear optical activity-based devices [1], SERS [2], solar cells [3], and much more.

Since the optical properties of the nanocomposites are particularly sensitive to the morphological properties of the embedded NPs, understanding their growth mechanism is crucial to generate nanocomposites with controlled properties.

Spectroscopic ellipsometry was previously used to monitor the growth silver NPs in polymer matrices. Voue et *al.* [4] performed ellipsometric measurements in the UV-near IR spectral range of the optical properties of AgNPs during their thermal growth in a PVA matrix. Oates et *al.* [5] have shown that the mean radius of the NPs can be determined by analyzing the ellipsometric spectra with the Maxwell Garnett theory. However, their approach does not consider the shape distribution of the NPs. These distributions lead to a misestimation of the value of the NPs radius. Recently, we have introduced a new effective medium theory named Shape Distributed Effective Medium Theory (SDEMT) to model the optical properties of a collection of ellipsoidal NPs which exhibits a shape distribution.[6]

The purpose of this study is to investigate the thermal growth of Ag NPs in PVA matrix by in-situ spectroscopic ellipsometry in the visible spectral range. Each spectrum is analyzed with the SDEMT model. This procedure allows the determination of the film thickness, the shape distribution and the volume fraction of the NPs as well as the effective dielectric function of the nanocomposite film during the annealing process at 110°C.

These parameters enable us to investigate the growth mechanism of silver NPs. We show that the films exhibit a plasmon resonance located at 450 nm, which progressively increases in amplitude during the annealing. Due to the evaporation of the solvent, the film thickness decreases by 15 nm during the annealing. The silver ion reduction and NPs growth occurs when the temperature is higher than 50°C. The NPs become rapidly spherical while a kinetic model can be used to describe the evolution of the volume fraction of NPs.

Our conclusions are validated by transmission electron microscopy images of NPs recorded after the growth process.

*[1] S. ANTHONY et al., J. Phys., **65**, 871-879, 2005.*
*[2] R. OMAR et al., J. Mater. Chem. C, **5**, 10813–10821, 2017.*
*[3] Y.H. JANG et al., Chem. Rev., **116**, 14982–15034, 2016.*
*[4] M. VOUE et al., Thin Solid Films, **519**, 2963-2967, 2011.*
*[5] T. W. H. OATES et al., J. Phys. Chem. C, **111**, 182-187, 2007.*
*[6] Y. BATTIE et al., J. Nanoparticle Res., **18**, 1-13, 2016.*