Thickness-dependent refractive index in plasmonic nanocomposites: a principal components and support vector machines analysis

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Nanocomposites made of polymer films embedding Ag nanoparticles were prepared by thermal annealing of poly-(vinyl) alcohol films containing $AgNO_3$. The plasmon resonance of such films was studied by spectroscopic ellipsometry. At constant doping-level, multivariate statistical analysis techniques show that thick (> 300 nm) and thin (< 30 nm) films optically behave in a different way.

Introduction

Optical properties of plasmonic nanocomposites are strongly influenced by the size, the shape and the dielectric environment of the embedded nanoparticles (NPs). A wide range of experimental methods is available for the synthesis of such materials. Besides the methods involving the synthesis of the NPs in a liquid medium, with or without further coating to prevent their aggregation (see e.g. [1–4] and the references therein) and their dispersion in a solid phase, NPs can be synthesized *in situ* following the irradiation or the thermal annealing of the solid phase. Reduction of the Ag^+ ions to Ag^0 in poly(vinyl alcohol) films (PVA). We report here on the influence the film thickness and on the silver doping of the nanocomposite films on the plasmon resonance parameters. More precisely, using multivariate analysis techniques, we compare the resonance parameters in thin and thick films at a given Ag-doping level.

Results and discussion

PVA films doped with $AgNO_3$ were prepared by spin coating on silicon wafer subtrates. The coating conditions were varied to obtain thin (< 30 nm) and thick (> 300 nm) films. The ratio [Ag]/[PVA] was also varied : 2.5% (w:w) and 25%(w:w). After annealing at 110°C, the optical properties were determined by spectroscopic ellipsometry. The presence of the Ag NPs, as shown by AFM, was unambiguous (Fig. 1). The resonance parameters (Λ_0, peak position – Γ_0, resonance width – A, resonance amplitude) were analyzed by principal components analysis (PCA) and were classified by support vector machines algorithms (SVM). SVM algorithms results (Fig. 2) show that thick and thin films behave differently at equivalent Ag doping. These difference are probably due to different spatial distributions of the in situ grown NPs in the thin (2D) and thick (3D) films.

Conclusions

In this study, we have measured the optical properties of plasmonic nanocomposites embedding Ag NPs. Using multivariate analysis, we have shown that the same polymer solution yielded different optical behaviors as a function of the film thickness.

Acknowledgements

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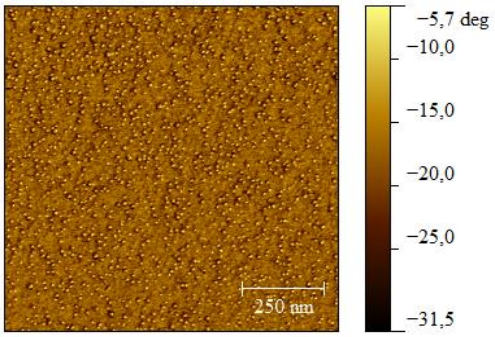

Fig. 1: Phase AFM images in intermittent contact mode of a Ag-PVA film doped with 25% $AgNO_3$ (w:w). (Thickness: 300 nm). Image size: 1 µm x 1 µm (256 x 256 pixels).

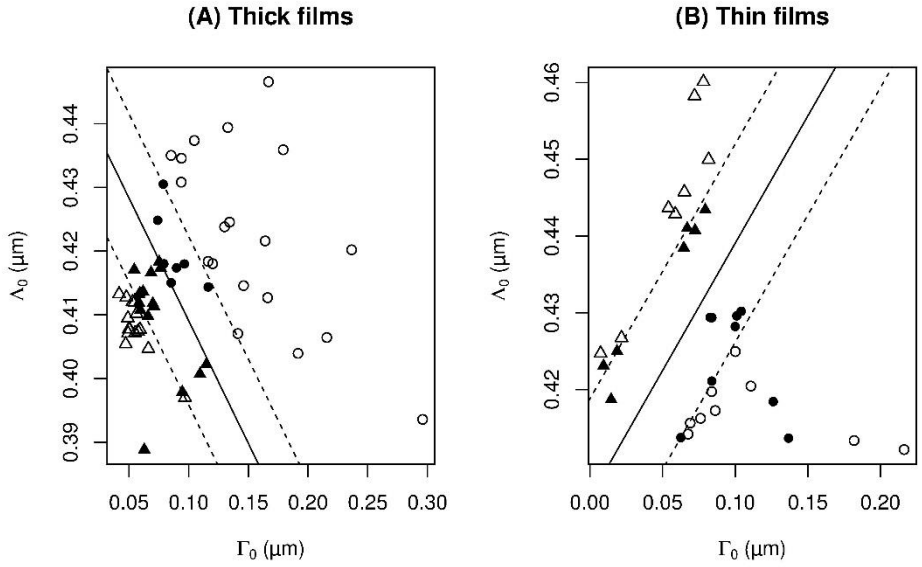

Fig. 2: Classification of the weakly and highly Ag-doped film in the $\Lambda_0 - \Gamma_0$ plane.
(A) Thick films (B) Thin films. Ag-PVA ratio: 25% (circles) and 2.5% (triangles) – Filled symbols: support vectors.

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