Effect of film thickness on the optical behavior of silver nanoparticles/polymer nanocomposite films

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Introduction

- Optical properties of metal nanoparticles (NPs) determined by a collective oscillation of the conduction electrons: surface plasmon polariton resonance (SPPR).
- Influence of the matrix on the SPPR: \( \varepsilon_{\text{Ag}}(\omega) = -2\varepsilon_{\text{PVA}}(\omega) \)
- In situ synthesis of the NPs in a poly(vinyl alcohol) (PVA) matrix by chemical reduction of the metal salt during thermal annealing of the film.
- Preparation of Ag-PVA films with high (25% w:w) and low doping levels (2.5% w:w) by spin-coating of the dried polymer solution on silicon wafers.

- Study of the film topography by AFM in true non-contact mode.
- Study of the optical properties by spectroscopic ellipsometry to simultaneously access to the thickness of the film and to the frequency-dependent dielectric function \( \varepsilon(\omega) = N^2(\omega) \).

Spectroscopic ellipsometry

Spectroscopic ellipsometry: Non-destructive optical analysis technique based on the relative change of polarization of the \( p \)- and \( s \)-components of the light at the interface between two media characterized by different optical properties:

\[
\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta} \quad \alpha = \cos(2\Psi) \quad \beta = \sin(2\Psi)\cos(\Delta)
\]

Table 1: Parameters of the plasmon absorption peak (\( A_0 \): amplitude of the absorption peak; \( \lambda_0 \): position of the resonance; \( \Delta_0 \): width of the resonance) as a function of the film thickness for highly doped PVA films (Ag/PVA ratio: 25% w:w). Data correspond to the optical properties presented in Fig. 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>( A_0 )</th>
<th>( \lambda_0 ) (nm)</th>
<th>( \Delta_0 ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin films</td>
<td>23.4 ± 0.2</td>
<td>0.145 ± 0.6</td>
<td>414.2 ± 0.7</td>
<td>67.6 ± 2.9</td>
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<tr>
<td></td>
<td>25.4 ± 0.3</td>
<td>0.131 ± 0.5</td>
<td>415.6 ± 0.6</td>
<td>69.0 ± 2.6</td>
</tr>
<tr>
<td>Thick films</td>
<td>305.9 ± 1.7</td>
<td>0.117 ± 0.2</td>
<td>405.4 ± 0.7</td>
<td>47.3 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>293.4 ± 1.7</td>
<td>0.118 ± 0.2</td>
<td>409.5 ± 0.6</td>
<td>49.2 ± 1.5</td>
</tr>
</tbody>
</table>

Optical properties of thick and thin films

Significant difference in the refractive index of thin and thick films at constant doping level.

Figure 1: AFM images of the polymer films topography (1 µm x 1 µm): A, pure PVA film; B, 25 nm thick doped film (Ag/PVA ratio: 2.5%); C, 25 nm thick doped film (Ag/PVA ratio: 25%); D, 290 nm thick doped film (Ag/PVA ratio: 25% w:w).

Figure 2: Ellipsometric spectra of Ag-PVA films (Ag/PVA ratio: 25% w:w): A, thin films (thickness: 25.4 nm); B, thick film (thickness: 293.9 nm). Experimental data: \( \alpha \) (filled circles) and \( \beta \) (open circles). Dashed lines: optimized results from the optical model.

Figure 3: Optical properties of thin (solid lines) and thick (dashed lines) silver NPs-doped PVA films (Ag/PVA ratio: 25% w:w): A, refractive index \( n \); B, extinction coefficient \( k \).

Figure 4: Resonance width versus resonance wavelength for PVA films with high (open symbols) and low Ag doping levels (plain symbols).

Conclusion and acknowledgements

- In situ synthesis of silver NPs by thermal annealing of a polymer film containing metal salt.
- Simultaneous determination of thickness and optical properties: SPPR localized at ~ 3 eV.
- High doping level (25% Ag): different behavior between thin and thick films (2D → 3D).

This work is financially supported by the National Fund for Scientific Research of Belgium (FRFC project n°1926111).