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Gold nanoparticles growing in a polymer matrix: What can we learn from spectroscopic imaging ellipsometry?

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ABSTRACT

Despite an increasing number of studies and the apparent simplicity of these model systems, the mechanisms of the growth of metal nanoparticles in a polymer matrix and, in particular, that of gold nanoparticles is still not fully understood. Usually, reported results concern global (ca. surface-averaged) measurements. Furthermore, the optical properties of plasmonic nanocomposites are difficult to investigate when the metal volume fraction is very low, typically less than 1%. This is especially true in the case of gold for which the localized plasmon resonance is less sharp than in the case of silver and, therefore, less easy to probe. In this article, the optical properties of gold-doped nanocomposites have been studied at the (sub)micrometer scale using spatially resolved spectroscopic ellipsometry. At low gold volume fraction, the thermal annealing of the composite leading to the in situ growth of the gold nanoparticles induces a local inhomogeneity of the Ψ and Δ ellipsometric images that can be analyzed in terms of heterogeneity of the gold fraction. Spectroscopic imaging ellipsometry confirms the existence of gold-depleted regions in the vicinity of the largest gold particles.

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I. INTRODUCTION

Since the pioneered work of LaMer and Dinegar,1 who were the first ones to propose an explanation for the growth mechanism of nanoparticles in solution, a significant number of studies have been carried out to assess this mechanism2 and to extend it to particles grown on solid surfaces by sputtering3 or inside a solid matrix, like a polymer matrix.4-6 The study of Ng et al.7 describes the properties of gold nanoparticles’ (AuNPs’) thin films on silicon (Si) substrates. AuNPs with different sizes and/or different aspect ratios were prepared using the seeding-growth method and deposited on Si substrates using a spin-coating method followed by heat treatment at 200 °C. In the study of Vieaud,4 the AuNPs were synthesized in aqueous solution before dispersion in a polymer solution and spin coating on a solid substrate, whereas in a recent study of Omar et al.,8 monodispersed gold nanocubes are synthesized by spin coating of a gold precursor-loaded polymethylmethacrylate dispersion on N-doped silicon. It is well known that embedding metal nanoparticles (NPs) in a dielectric matrix modifies numerous physicochemical properties of the materials. The main effects are observed on the optical properties. One of these, the localized surface plasmon resonance (LSPR), is due to the collective oscillations of the conduction electrons of the NPs caused by the excitation of the electromagnetic field associated with the propagation of light.9 There are numerous experimental ways to synthesize such plasmonic nanocomposites. Compared to the conventional synthesis of gold colloids by the Frens-Turkevitch method10 and their dispersion in a host matrix, the “one-pot” synthesis appears to be an easier method to manufacture plasmonic nanocomposite materials. It provides the opportunity of preparing at once thin films with a larger NPs concentration than in solution. This method is derived from the polyol method. A noble
metal in one of its salt forms (HAuCl₄) is mixed with the polymer solution that plays the reducing agent and helps the stabilization of the NPs during and after the thermal annealing of the film.

Contrary to plasmonic nanocomposites containing in situ grown silver nanoparticles, gold nanoparticles (AuNPs) synthesized in situ in a polymer matrix are not a subject often discussed in the literature despite the simplicity of the synthesis. Moreover, experimental procedures strongly differ from one publication to the other, making their results very difficult to compare. Nevertheless, Porel et al. showed the possibility of forming polygonal nanoplates in a polymer matrix. Sun et al. analyzed the optical properties of a poly-(vinyl alcohol) (PVA) film embedded with AuNPs in situ grown by thermal annealing. Sakamoto et al. used laser irradiation as an alternative method to generate the AuNPs in the PVA matrix. With ellipsometry as a nondestructive optical technique to analyze nanocomposites, the doping level of the polymer by the metal is a cornerstone parameter that plays a central role in probing the changes in the optical properties of the films. Vieuud presented an excellent work on the properties of AuNPs in PVA but the volume fraction of gold is higher than 5%. More recently, Battie et al. have developed a new numerical method to determine the parameters of the shape statistical distribution of plasmonic nanocrystals. The lowest volume fraction used in their publication is 0.7%.

In a recent publication, we have shown that the growth of AuNPs at a low doping level (a volume fraction of around 0.13%) in a PVA matrix occurs according to a two-step process which is evidenced by a change of the optical properties of the nanocomposite film during the annealing. More precisely, the largest particles are surrounded by polymer film regions whose optical response is clearly different from that of the background. Such films containing low metal volume fractions could find their applications as passive Q-switch due to the nonlinear optical properties of the nanocomposite, or as amplifying medium in random lasers when associated with Rhodamine 6G, for instance.

In this paper, we try to provide additional information about the AuNPs growth in polymer films, and we report on the local spectroscopic characterization of these films. We also compare the analysis carried out by conventional spectroscopic ellipsometry and by spectroscopic imaging ellipsometry. In other words, we will try to explain the added value of a local analysis of the optical properties in this specific case. To the best of our knowledge, such results on the local optical response of Au-PVA films have never been reported.

II. EXPERIMENT

HAuCl₄ and poly(vinyl alcohol) (PVA, 87%–89% hydrolyzed, MW 13k–23k) were purchased from Sigma-Aldrich and used as received. All the synthesis was done using 18 MΩ MilliQ water. Au-PVA nanocomposite films were prepared using the experimental protocol for Ag-PVA films from Ramesh et al. with some changes like the metal salt and the spinning conditions to achieve the required thickness range and the metal doping level. As previously described, aqueous stock solutions of PVA (10% w/w) and of 0.1 M HAuCl₄ were prepared. These stock solutions were mixed together in adequate proportions to finally obtain a 8% w/w polymer solution with a 2% Au/PVA mass ratio. After RCA cleaning, (100) Si wafer fragments were coated with that solution using a Laurell WS-650-23B spin-coater, typically at 2500 rpm during 90 s. The mass ratio of 2% of gold in a polymer corresponds to a volume fraction of fAu = 0.13% in the dry film.

Spectroscopic imaging ellipsometry (SIE) measurements of the ellipsometric angles Ψ and Δ were performed on Au-PVA thin films spin coated on Si substrates with an EP3-SE spectroscopic nulling ellipsometer (Accurion GmbH, Gottingen). The objective of the EP3 was a Nikon CF Plan SLWD 10X objective (NA = 0.21). The wavelength range was 360–1000 nm, and the measurements were carried out at three different angles of incidence (AOI) (45°, 55°, and 65°), as a function of the analysis type. Imaging ellipsometry techniques have been extensively used to explore the local optical properties of the thin films, namely, the complex dielectric function and the absorption coefficient along with the film thickness and roughness. Multiple regions of the sample were investigated at once, allowing us to record the local optical behavior. Data were processed using the EP4 software (Accurion GmbH). The spatial resolution was 1.07 × 1.07 μm² per pixel at 45° of incidence.

Conventional spectroscopic ellipsometry (SE) measurements were performed with a SOPRA GESP5 spectroscopic ellipsometer in parallel beam configuration and at an angle of incidence of 70°. The small diameter of the spot on the sample was about 4 mm. The SE data were processed using the Winelli software.

To induce the growth of the AuNPS, the samples were annealed using a THMS600 Linkam heating/cooling stage. The temperature was raised from room temperature (around 23 °C) to 135 °C at the heating rate of 10 °C per minute. After that, a plateau value was maintained to achieve an experiment duration of 120 min. Thermal fluctuations were less than 0.1 °C.

III. RESULTS AND DISCUSSION

A. Optical models

Two optical models were used to analyze our ellipsometric data.

1. Model 1

As in our previous articles and due to its high transparency in the visible range, the optical properties of the polymer film are adequately described by a Cauchy law for the index of refraction n(λ), with the extinction coefficient k(λ) being set to 0. The undoped PVA samples are, therefore, described by a two-layer model, including the polymer film, the native oxide layer, and the (100) silicon substrate. The thickness of the native silicon oxide layer is 2 nm and was not optimized throughout the rest of our study.

2. Model 2

Effects of the metal nanoparticles embedded in a polymer film on the composite film optical properties can be described from different theories. They have been reviewed by Oates et al. and their key points will be briefly reminded hereafter. A spherical solution to Maxwell’s equations was presented by Mie, which accurately predicts the resonance frequency of spherical metal particles. This approach is commonly used within the quasistatic approximation for which only dipolar resonance is observed. In the dipolar-dominated small
size limit, the particle may be considered as a classical oscillating dipole and the absorbed photons are thus efficiently reradiated. Mie theory results are quite often compared to the results of effective medium approximation (EMA) theories. As quoted by Oates et al., the Maxwell-Garnett EMA (MG-EMA) uses “the Rayleigh formulas and takes the first order approximation of this relation, i.e., all particles give a similar change to the dielectric function and the change in the dielectric function of the host is negligible with the inclusion of more particles.” Although the Mie theory is a “single particle” theory, it is commonly used to describe the optical properties of colloidal solutions and the limit that would determine the use of either the Mie theory or MG-EMA is not clearly defined. In this study, the number of particles per unit of volume is sufficiently large to consider the use of the MG-EMA in the analysis of our data. To analyze the optical response of the plasmonic nanocomposites after annealing, a second optical model was proposed, as follows. The Cauchy dispersion law parameters determined on the undoped film are kept constant (negligible effect of the particles on the polymer matrix itself), and a gold volume fraction \( f_{Au} \) is accounted within the Maxwell-Garnett effective medium approximation (MG-EMA) according to

\[
\frac{\epsilon_{eff} - \epsilon_{Au}}{\epsilon_{eff} + 2\epsilon_{Au}} = f_{Au} \frac{\epsilon_{PVA} - \epsilon_{Au}}{\epsilon_{PVA} + 2\epsilon_{Au}},
\]

where \( \epsilon_{Au} \), \( \epsilon_{PVA} \), and \( \epsilon_{eff} \) are the complex dielectric functions of gold, the polymer matrix, and the nanocomposite film, respectively.

This approach for data analysis is a standard approach in ellipsometry to account for the contribution of spherical inclusions at low volume fractions. Furthermore, in the limit of very small \( f_{Au} \), the MG-EMA converges to the quasistatic Mie case. This applies, in particular, to the AuNPs and the volume fractions considered in our study.

These models are schematically represented in Fig. 1. The optical constants of crystalline silicon and silicon dioxide are well known and were obtained from classical optical databases.

B. Global optical properties obtained by conventional spectroscopic ellipsometry

Au-PVA films have been prepared by spin coating on silicon substrates at a low gold-doping level (2% w/w Au/PVA). The spinning conditions were adjusted in a view of obtaining films whose thickness was in the range of 300–500 nm. The metal mass fraction corresponds to a volume fraction of \( f_{Au} = 0.13\% \). The films were annealed at 135°C and after cooling down to room temperature. Control experiments of doped films deposited on glass have been performed to confirm the growth of the nanoparticles by UV-Vis spectroscopy. The samples became reddish at the end of the annealing. The optical transmission showed an LSPR absorption peak near 530 nm with a full width at half maximum around 50 nm. No other peak was found assessing the validity of the quasi-static approximation. On the basis of AFM images published in our precedent study, we can attribute this absorption peak to AuNPs with a diameter of 40 nm approximately. The ellipsometric angles \( \Psi \) and \( \Delta \) were measured in the 1.5–4.0 eV energy range with a Sopra GESP5 ellipsometer. Control experiments have been carried out on undoped films under similar experimental conditions.

The ellipsometric data are presented as \( \alpha = \cos(2\Psi) \) (open symbols) and \( \beta = \sin(2\Psi)\cos(\Delta) \) (closed symbols) in Fig. 2. For clarity, only one experimental point over 10 is drawn in the figure. For the undoped samples [Fig. 2(a)], the optimized thickness is 358.1 ± 0.1 nm and the optimized spectra are in excellent agreement with the experimental data [root-mean-squared error (RMSE) = 1.49 × 10⁻³]. As the annealing of the samples at 135°C (i.e., above the glass transition of the polymer, \( T_g = 85°C \)) promotes the growth of the AuNPs in the film, the \( \alpha \) and \( \beta \) spectra were analyzed on the basis of the second model, i.e., including the contribution of the nanoparticles to the dielectric function via the MG-EMA. In this model, the thickness of the film and the gold volume fraction \( f_{Au} \) were the adjustable parameters. After optimization of the ellipsometric data [Fig. 2(b)] using Model 2, the thickness of the film was found to be 441.8 ± 0.1 nm and \( f_{Au} \) was 2.6×10⁻³ ± 2.9×10⁻³%, a value much lower than the one expected on the basis of the experimental protocols (\( f_{Au} = 0.13\% \)). Moreover, the relative error on the gold fraction is higher than 110%, which means that this result is not statistically relevant. No specific feature is seen in the ellipsometric spectra at about 2.33 eV, the energy of the localized plasmon as determined from the Fröhlich equation and the complex refractive index of both gold and PVA. Furthermore, the optimization can be carried out using Model 1, ca. without taking into account the gold contribution, yielding comparable thickness (441.9 ± 0.1 nm) and RMSE (2.019×10⁻³). It is, therefore, evident that conventional SE does not allow us to distinguish between the undoped and the doped samples at such a low gold-to-polymer mass ratio. The main reasons for this lack of success in the modeling have probably to be sought in the spatial averaging of the optical response over the measurement spot area and of the local heterogeneity of the samples in thickness and chemical composition, as highlighted in our recent publication.

C. Imaging ellipsometry of the AuNPs growth

Imaging ellipsometry allowed us to bypass these drawbacks and let us access to the local optical response. Because the size of the pixels in the \( \Psi \) and \( \Delta \) maps obtained with the SIE was 1.07μm, the lateral resolution is improved by a factor of 4000 compared to the conventional SE for which the lateral dimension of the spot on the sample was ca. 4 μm.
When operated in the mapping mode, the imaging ellipsometer allows us to perform statistics on the $\Psi$ and $\Delta$ values of the sample over a large number of data (typically ca. $120 \times 10^3$) and, therefore, to obtain statistical distributions of the ellipsometric angle values. On spatially uniform and homogeneous samples (i.e., in the absence of thickness gradients or of materials change), it appears that these statistical distributions are Gaussian ones due to the measurement process. On nonideal samples, the width of the Gaussian depends on its surface state (including its roughness) and on the size of the region-of-interest over which the measurement is carried out. The smaller the region, the smaller the width of the statistical distribution. In conventional SE experiments, these local statistical fluctuations are averaged over the spot size. From a practical point of view, any deviation from this Gaussian statistical distribution of $\Psi$ and $\Delta$ values is, therefore, a clue of some inhomogeneity (either structural or optical) of the sample. As shown in our recent work, the optical response is spatially homogeneous at the beginning of the annealing procedure and the growth of the nanoparticles induces heterogeneity as clearly seen in Fig. 3. The histogram of the ellipsometric angles cannot be described by a single Gaussian. It has to be deconvoluted and is well fitted by the sum of three Gaussian peaks [Fig. 4(d)]. The sum of two Gaussian peaks was also tested but the RMSE was more than two times higher than in the retained option (two peaks: RMSE = 3.13; three peaks: RMSE = 1.35).

A shoulder appears at the right of the maximum near 184°. This value was chosen to threshold the image ($T_2$) and the rightmost tail of the distribution was chosen for $\Delta > 187°$ ($T_1$). On the basis of these two threshold values $T_1$ and $T_2$, we were able to define three sets of pixels at the end of the annealing [Fig. 4(d)] and to follow their mean values as a function of the time (Fig. 5). The curves are similar to each other during the first 60 min of the experiments, confirming the homogeneity of the sample until the end of this period. Afterwards, the average value in the region $\Delta < T_1$ starts to decrease. The most striking feature is the strong divergence of the curves for $t > 90$ min. This can be related to the study of Guyot et al. (Figs. 10 and 11), where it was shown that the standard deviation of the $\Delta$ and $\Psi$ statistical distributions strongly increased at that time. As a reminder, the behavior of the $\Delta$ values is complex during the first ten minutes due to the residual solvent evaporation, the relaxation of the mechanical constraints induced by the spin coating and the glass transition temperature of the polymer.
D. Local optical properties of the Au-PVA thin films

Based on the nulling concept, the polarizer and analyzer of the ellipsometer can be rotated, respectively, to each other in the way of enhancing the contrast of the images, prior to the determination of the optical response in terms of ellipsometric angles $\Psi$ and $\Delta$. This technique is usually referred to as ellipsometric enhanced contrast microscopy. A typical ellipsometric enhanced contrast image taken at 533 nm is presented in Fig. 6 and clearly reveals the heterogeneity of the optical response.

To strengthen our analysis, ellipsometric $\Psi$ and $\Delta$ maps have been measured in the 360–1000 nm spectral range. Some of them are presented in Fig. 7 for $\lambda = 533, 660, $ and 920 nm. The wavelengths have been chosen close to the resonance (533 nm) and far from it (920 nm). The third one was chosen for the purpose of comparison with our previous study13 (658 nm). The contrast of the images is strongly influenced by the wavelength but also depends on the choice of the ellipsometric angle ($\Psi$ and $\Delta$). Images obtained in the NIR region only bring little information about the optical response heterogeneity.

To take into account the heterogeneity of the optical response, ellipsometric spectra in $\Psi$ and $\Delta$ have been measured in two different regions-of-interest labeled ROI0 and ROI1 as indicated by the rectangles in Fig. 6. The ellipsometric spectra are presented in Fig. 8. The insets in the top and bottom panels of Fig. 8 show the details of the ellipsometric response in the plasmonic band region (500–600 nm). Although the data coincide with each other for wavelengths less than 400 nm and higher than 700 nm, they appear to be slightly shifted in the spectral domain where the LSPR has to be found. The insets of Figs. 8(a) and 8(b) enhance the details of this effect.

As already done in the case of conventional SE data, the SIE data were analyzed on the basis of our second model, ca. including a MG-EMA contribution to the dielectric function of the nanocomposite layer and fitting on both the thickness of the layer and its gold volume fraction. The optical properties of
the polymer matrix is well described by a Cauchy dispersion law (Appendix). The values of $A_n$ and $B_n$ are fixed for the MG-EMA used in the second optical model. For both ROIs, Model 2 adequately describes the experimental data. The best-fit parameters as well as the RMSE are given in Table I. The correlation coefficients between the thickness of the film and the gold volume fraction $f_{Au}$ in the film are $-0.769$ and $-0.742$ for ROI0 and ROI1, respectively. The thickness in the different ROIs is slightly different but this difference cannot completely explain the shift between the $\Psi$ and $\Delta$ curves. The gold volume fraction $f_{Au}$ is significantly higher in ROI1 ($f_{Au} = 0.103 \pm 0.013$) than in ROI0 ($f_{Au} = 0.006 \pm 0.013$). $f_{Au}$ of ROI0 is not statistically relevant as its relative error is around 216%, and this result could be equivalently associated with a null volume fraction of gold in the polymer in this area. The heterogeneity of the optical response can, therefore, be attributed to a local change of the metal fraction. Our results also show that the growth of the gold NPs inhomogeneously occurs in the polymer matrix. Furthermore, our results demonstrate the possibility of detecting gold-doping with SIE at low concentration. Due to the (sub)micrometer scale analysis of our Au-PVA nanocomposites, we are able to detect a volume fraction of gold of around 0.1%, while the volume fraction detected by a conventional ellipsometer is usually recognized to be higher than 1% in thin films. At a lower doping level, corresponding to a volume fraction of 0.06%, the optical properties of Au-PVA nanocomposites do not significantly differ from those of a pure PVA film. It seems that a gold-doping level of 0.10% is rather close to the lower limit of detection of the technique.

From the $\Psi$ and $\Delta$ ellipsometric maps measured near the LSPR wavelength ($\lambda = 533$ nm), it has been possible to calculate using Model 2 both the local thickness of the layer $d(x, y)$ and the local gold fraction $f_{Au}(x, y)$ for each pixel of the image. The starting parameters of the optimization were the parameters obtained by our SIE analysis over ROIs 0 and 1 (Table I). These results as well as the relative error on $f_{Au}$ are given in Figs. 9(a)–9(c). During the numerical inversion of the ellipsometric equations, the parameters were
constraint as follows: $300 \text{ nm} \leq d \leq 400 \text{ nm}$ and $0\% \leq f_{Au} \leq 1\%$. From the comparison between Figs. 6 and 9(a), it appears that the regions with the same color than the ROI$_1$ in Fig. 6 are regions for which $f_{Au}$ is significantly different from zero and that the relative

<table>
<thead>
<tr>
<th>ROI</th>
<th>Thickness (nm)</th>
<th>Gold fraction $f_{Au}$ (%)</th>
<th>RMSE</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>359.8 ± 0.2</td>
<td>0.006 ± 0.013</td>
<td>0.682</td>
<td>−0.736</td>
</tr>
<tr>
<td>1</td>
<td>360.8 ± 0.1</td>
<td>0.103 ± 0.013</td>
<td>0.688</td>
<td>−0.730</td>
</tr>
</tbody>
</table>

From the comparison between Figs. 6 and 9(a), it appears that the regions with the same color than the ROI$_1$ in Fig. 6 are regions for which $f_{Au}$ is significantly different from zero and that the relative
error on $f_{Au}$ is small contrary to the remaining part of the image ($f_{Au} \simeq 0$) for which the associated relative error is several orders of magnitude larger [red regions in Fig. 9(b)]. This can be explained by local values of $f_{Au}$ close to the lower bound imposed on the optimization algorithm and the lack of significance of this parameter in these regions (almost undoped polymer). The thickness map [Fig. 9(c)] does not reveal specific features. Additional analysis of the data presented in Fig. 8 to include surface roughness or void inclusions in the models was not conclusive. The thickness and the metal volume fraction presented in Fig. 9 have also been plotted as a function of each other, without providing us additional significant information on their correlation. This leads us to conclude that the main effect of the annealing of the film is a modification of the local refractive index due to the increase of the gold volume fraction in some regions of the film.

IV. CONCLUSIONS

In this article, we presented an experimental study of the optical properties of gold-doped nanocomposites using spectroscopic imaging ellipsometry. We have found that, for a thin polymer film ($d < 500$ nm) and at a low gold-doping level ($f_{Au} < 0.2\%$), the growth of the AuNPs inhomogeneously occurred within the film. At this low doping level, the optical constant determined by the conventional spectroscopic ellipsometry spectra is only relevant for the polymer matrix. We have also shown the advantage of using spatially resolved spectroscopic ellipsometry by choosing areas on the image with a different intensity contrast. The ellipsometric spectra of each region of interest were different, especially between 400 and 600 nm, the spectral region corresponding to the localized surface plasmon resonance of gold nanoparticles. Using the MG-EMA model, we showed that each zone presents a point-to-point variation of the optical response of film 2 was only optimized with respect to the film thickness to validate the optical properties of the material. The optical response of film 2 was only optimized with respect to the film thickness to validate the optical properties of the material. The optimization results are presented in Fig. 10. The adjusted thickness is 266.1 ± 0.1 nm, with an RMSE equal to 1.858. For both films, the simulated spectra are in very good agreement with the experimental data.

Typically, film 1 and film 2 were obtained with the following spinning parameters: 2000 rpm, 90 s and 6000 rpm, 90 s, respectively. The ellipsometric angles $\Psi$ and $\Delta$ were measured using an EP3-SE spectroscopic ellipsometer. The refractive index and the thickness of the film were determined for film 1 using a Cauchy dispersion law,

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2},$$

where $A_n$ and $B_n$ are the Cauchy coefficients. Optimized parameters were $A_n = 1.509 \pm 0.002$ and $B_n = 3172 \pm 296$ nm$^2$ (RMSE = 0.966). The thickness of the film was 365.2 ± 0.6 nm. The optical response of film 2 was only optimized with respect to the film thickness to validate the optical properties of the material. The optimization results are presented in Fig. 10. The adjusted thickness is 266.1 ± 0.1 nm, with an RMSE equal to 1.858. For both films, the simulated spectra are in very good agreement with the experimental data.

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