Real time spectroscopic ellipsometry of nanoparticle growth

T. W. H. Oates\textsuperscript{a)}

Forschungszentrum Rossendorf, Institute of Ion Beam Physics and Materials Research, P.O. Box 510119, Dresden D-01314, Germany

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The use of real time spectroscopic ellipsometry to study silver nanoparticle formation in a polystyrene matrix by temperature induced reduction of silver hexafluoroacetylacetonate is reported. The optical properties of the composite are modeled using Mie theory with a modified electron relaxation frequency in silver to account for particle size effects. By measuring the final particle sizes from electron microscopy, the size of the particles during growth can be inferred above a radius of 2.3 nm. Below this radius the model is limited by quantum effects. © 2006 American Institute of Physics. [DOI: 10.1063/1.2206870]

Noble metal nanoparticles exhibit strong plasmon polariton resonances, a feature that is increasingly utilized in biosensor and optoelectronic applications.\textsuperscript{1} It has been shown that it is experimentally possible to relate the broadening of the plasmon resonance with the average size of the nanoparticles by assuming that the dominant contribution to the broadening arises from electron scattering at the particle boundary.\textsuperscript{2} By determining the particle diameters from electron micrographs the broadening can be scaled to provide a method of determining the size of the nanoparticle from the optical absorption. Recent advances in spectroscopic ellipsometry (SE) hardware and software make it possible to record in real time changes in optical properties of thin films and overlayers, making it ideal for the study of ultrathin polymer metal nanoparticle composites. SE has been used to determine the size and concentration of embedded copper and gold nanoparticles.\textsuperscript{3,4} We recently reported the use of real time in situ spectroscopic ellipsometry to study the growth of silver nanoparticles on SiO\textsubscript{2} by magnetron sputtering of silver.\textsuperscript{5} The present work examines in real time the growth of silver nanoparticles in a polymer matrix using spectroscopic ellipsometry.

For this study, 0.12 ml of 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac) (Sigma Aldrich) was mixed with a suspension of 0.15 g of Ag\textsubscript{2}O (Sigma Aldrich) in 15 ml of toluene (Sigma Aldrich), producing a complex of Ag(hfac)(toluene).\textsuperscript{6} 0.3 ml of this solution was then mixed with 1 ml of 1% poly styrene (BASF) in toluene. Polystyrene films (ca. 50 nm thick) containing 3% (w/w) of silver in the form of Ag(hfac) were formed on silicon wafers by spin coating at 3000 rpm for 1 min. After drying the samples were placed on a boron electric heater with an attached thermocouple. This arrangement was aligned in the beam of a J.A.Woollam M2000 rotating-compensator spectroscopic ellipsometer\textsuperscript{7} at 75° incident angle with a spectral range from 1.3 to 3.3 eV. Spectroscopic data (399 wavelengths) were collected every 5.4 s as the sample was heated to 250 °C.

In the first 3 min of heating the Ag(hfac) decomposed around 120 °C with a concomitant formation of silver nanoparticles. Further heating began to melt the polymer around 180° followed by evaporation above 220°. After 30 min there was an abrupt change in the ellipsometric parameters indicating the complete evaporation of the polymer, leaving exposed silver nanoparticles on the silicon surface. While the literature values for the glass transition temperature and melting point of polystyrene are 100° and 240°, respectively, in ultrathin films these values are dependent on the film thickness and substrate surface energy.\textsuperscript{8} The exposed particles were imaged with scanning electron microscopy (SEM) to determine the particle size distribution. For transmission electron microscopy (TEM) analysis a second sample was prepared with a TEM grid on the silicon surface. The heating was stopped at 140 °C, leaving the particles embedded in the polymer.

Figure 1(a) shows a TEM image of a typical nanoparticle in the polymer film. Approximately spherical and 15 nm in diameter, the particle consists of a single fcc crystallite with a lattice constant of 0.409 nm. The majority of particles were observed to consist of a single crystallite. For the ellipsometric analysis presented below we assume that the particles are single crystals and that electron scattering is dominated by collisions with the particle boundaries. Figure 1(b) shows a SEM image of the nanoparticles on the silicon surface, while 1(c) is a size histogram of 501 particles, showing an average particle diameter of 14.8 (±0.1) nm with a standard deviation

\textsuperscript{a)Electronic mail: t.oates@fz-rossendorf.de}

FIG. 1. (a) TEM image of a silver nanoparticle embedded in polystyrene matrix. The particle is an approximately spherical single crystal of radius 7.5 nm; (b) SEM image of exposed nanoparticles following the complete evaporation of the polymer matrix. (c) Particle sizes measured from the SEM image.
of 7.5 nm. The histogram shows a Gaussian distribution around 10 nm with an extended tail which suggests that some of the particle may have combined during the polymer evaporation phase, forming larger particles and increasing the average size. X-ray diffraction (XRD) was employed using the Scherrer equation on the Ag(111) peak, supporting the SEM data with an average crystal size of 14.1 nm.

The ellipsometric data are fitted using the Maxwell-Garnett effective medium approximation (MG-EMA) which is the limiting case for Mie resonances when the particles are small compared to the wavelength of light (ca. \( R < 10 \) nm) (i.e., only the dipolar plasmon resonance is considered).\(^2\) A parametric nonabsorbing two-parameter Cauchy model was used for the polymer matrix. For the first 10 min the Cauchy parameters remained within the range of a pure polymer film subjected to the same heat treatment (2.35 < \( \varepsilon_1 < 2.9 \)) until the polymer began to melt and finally evaporate. Silver optical constants were modeled using the Drude free-electron equation\(^1\)

\[
\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 - i\Gamma \omega} ,
\]

where \( \omega_p \) is the bulk plasma frequency, \( \Gamma \) is the free-electron relaxation frequency, and \( \varepsilon_\infty \) is the contribution from interband transitions. For particles smaller than the mean free path of electrons in the bulk, \( \Gamma \) is inversely proportional to \( R \) and can be described by\(^11\)

\[
\Gamma = \Gamma_B + \frac{A \nu_F}{R} ,
\]

where \( \Gamma_B \) is the bulk free-electron relaxation frequency, \( \nu_F \) is the Fermi velocity for silver (1.39 \( \times 10^6 \) cm/s), and \( A \) is a constant of proportionality which must be determined by comparison with microstructural analysis. The parameters \( \varepsilon_\infty, \omega_p, \) and \( \Gamma_B \) for silver were determined by fitting Eq. (1) to the data from Johnson and Christy\(^12\) (4.124, 9.22, and 0.022 eV, respectively).

To determine the value of \( \Gamma \), the ellipsometric data at the 5 min point were fitted with the above model using five fitting parameters: film thickness, percentage content of silver, \( \Gamma \), and the two Cauchy parameters. A film thickness of 38 nm and a silver content of 1.8% were obtained with \( \Gamma = 0.39 \) eV. Figure 2(a) shows the agreement between the experimental and generated data (including the silicon substrate). Figure 2(b) shows the dielectric constants of the composite film from the fitted data with the prominent plasmon polariton absorption at 3.0 eV. \( \Gamma \) and \( R \) (from the SEM image) are now used in Eq. (2) to give \( A = 0.47 \). Since \( A \) is a matrix dependent parameter it can only be compared qualitatively with literature values. Reviews can be found in Refs. 13 and 14, giving theoretical values from 0.29 to 1, while experimental values from 0.15 to 3.6 have been reported.\(^13,13,15\)

Real time data were fitted using the above model for the first 10 min of heating. After this, large variations in the polymer optical properties due to evaporation complicated the modeling. The thickness and silver fraction of the film up to 10 min are shown in Fig. 3(a). Initially the film thickness increases marginally due to thermal expansion before a reduction in film thickness during the nanoparticle formation, explained by the outgassing of volatile components of the organometallic precursor. Figure 3(b) shows \( \Gamma \) and the particle radius determined using the predetermined value for \( A \). The main point of interest is that the particle size is observed to increase after 1.5 min from a radius of 2.3 nm to a value of 7.4 nm before reducing slightly due to heating effects to 6.4 nm. Heating effects manifest as an increase in electron-phonon scattering in the particles, thus increasing \( \Gamma_B \) in (2), with the effect of reducing the calculated value of \( R \). Heating
effects are expected to influence the values of particle radius by only a few percent during the particle formation. The change in $\Gamma$ as the composite film was cooled from 140° to room temperature was 0.01 eV or 2%.

The inability of the model to provide a reasonable estimate for the particle size below 2 nm is primarily due to particle size effects influencing the conduction band in the particle. Doremus and Rao have shown that for gold particles of $R < 2$ nm the plasmon band begins to spread out and is completely invisible in particles of 0.5 nm in radius (ca. 31 atoms). The influence of a shift in the interband transitions, considered for a similar system by See et al., is also expected to play a minor role. It has been shown that for gold particles smaller than ca. 2 nm the interband transitions deviate from those in the bulk. Although the model requires further complexity to follow the growth of smaller particles, it is interesting to note that the values of film thickness and silver content remain reasonable in the early stages.

To conclude, a method is introduced to determine the size of nanoparticles in real time for particles in the size range of 2.3–10 nm in radius. The method opens possibilities to study the kinetics of particle formation. Refinement of the particle size determination from electron micrographs and XRD would be advantageous to further define the value of $A$. This would also be aided by a narrower particle size distribution.

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