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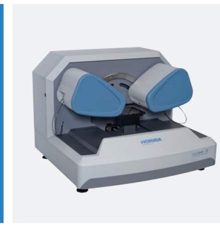
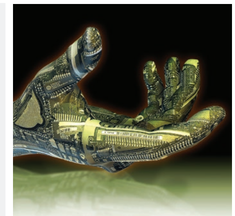
Spectroscopic Ellipsometry

Ellipsometric Characterization and Modeling of Different Types of Nanoparticles





Application Note

Material Science SE36

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Keywords: Nanoparticles, metamaterials, ellipsometric modeling, effective medium theory, spectroscopic ellipsometry

Abstract

UVISEL ellipsometers have been used for the characterization of several systems of nanoparticles. This ellipsometric characterization involves the development of specific modeling tools available within DeltaPsi2 software.

Introduction

Nanoparticles are of great scientific interest as they are a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale. Nanoparticles, defined as particle of any shape with dimension in the 1 to 100 nm range, often possess unexpected optical properties as they are small enough to confine their electrons and can produce specific so called plasmonic effects. For example, gold nanoparticles appear deep-red in solution. Another example relates to absorption of solar radiation that is much higher in materials composed of nanoparticles than it is in thin films of continuous material. One should also mention the trends of photonic crystals or optical metamaterials and their promising properties where ordered structures are achieved by arrangement of nanostructures. Thus, in many applications, controlling the size and shape of the particles, is of crucial importance.
This note illustrates the characterization of several systems of nanoparticles with UVISEL ellipsometers. This characterization involves modeling tools available within DeltaPsi2.

Maxwell-Garnett Effective Medium Theory: Application to Gold Spherical Nanoparticles in Polymer Matrix

In the first sample illustrated by this note, the nanoparticles have been included into PVA thin films deposited on silicon. The nanoparticles made of gold were synthetized by the Turkevitch method and their shape was spherical in the range of 14 nm in diameter. The following picture (fig 1.) illustrates typical surface topography of such samples.

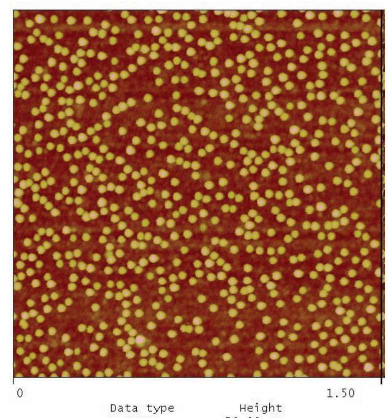

Figure 1: AFM picture of composite layer of Gold nanoparticles into PVA matrix

Optical properties of this kind of composite are calculated with the Effective Medium Theory (EMT). For this specific case of low concentration of metallic nanoparticles into a dielectric matrix, the Maxwell-Garnett model is the reference EMT. It gives an expression for dielectric function for the mixture, ε_{eff}, that is dependent on:

- Nanoparticle volume fraction f
- Dielectric function of both nanoparticle inclusions ε_i and ε_h

The range of validity of the EMT for such composite materials requires the nanoparticles to be much smaller than the wavelength of the probing beam. This approximation is also called the quasistatic limit, and the electric field is considered homogeneous inside the particle. One can notice that, following this restriction, the EMT is not sensitive to nanoparticle size. When particles are spherical, the Maxwell-Garnett expression for ε_{eff} is:

$$\frac{\varepsilon_{eff} - \varepsilon_h}{\varepsilon_{eff} + 2\,\varepsilon_h} = f\,\frac{\varepsilon_{np} - \varepsilon_h}{\varepsilon_{np} + 2\,\varepsilon_h} \qquad (1)$$

Using this approach, ellipsometric modeling for the sample is illustrated below (fig 2.). The theoretical data (blue line) fits only the experimental data (black dots) approximately.

The particle plasmon phenomena at 2.25 eV, responsible for the red color of gold nanoparticle solutions, is too intense in the theoretical curve. An improvement of modeling obtained on the red curve is achieved **by applying an electronic confinement correction** in the model. This correction takes into account a size effect of the nanoparticle and its influence on its optical properties.

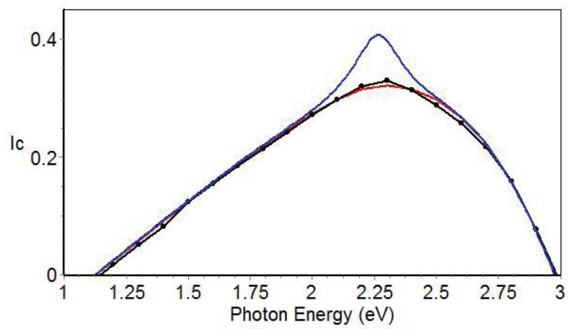

Figure 2: Modeling sample illustrated on Fig1. Experimental data in black dots, standard EMT modeling in blue, improved modeling with electronic confinement in red

The electronic confinement (fig 3.) occurs when the size of the nanoparticle becomes smaller than the mean free path of the electron under bulk conditions.

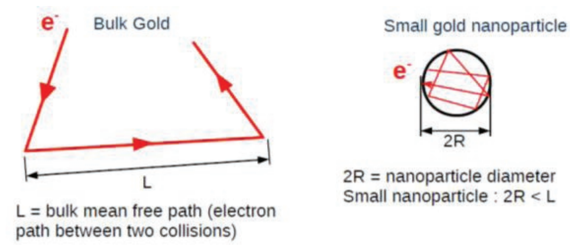

Figure 3: Illustration of electronic confinement

DeltaPsi2 handles this situation with advanced dispersion models where the effect of size is taken into account. The analysis follows a 3 step sequence:

- Determination of dielectric function of the effective medium (equation 1)
- Extraction of the dieletric function of the nanoparticle (equation 2)
- Determination of l_{NP} that gives theoretically access to the size of the nanoparticle. l_{NP} = 2R in the picture above and A and Fermi velocity, V_F, are characteristics for each material.

$$\varepsilon_{NP} = \varepsilon_{\infty\_Bulk} + \varepsilon_{interband\_Bulk} - \frac{\omega^2_{P\_Bulk}}{\omega^2 + i\omega\left(\Gamma_{Bulk} + \frac{Av_F}{l_{NP}}\right)} \qquad (2)$$

Generalizing Maxwell-Garnett for Non-Spherical Shapes: Application to Ag Nanowires

The Maxwell–Garnett formula given above (1) is valid for spherical inclusions in low concentrations, below approximately 10%. When the particles are not spherical anymore, but are elongated or flattened, respectively prolate or oblate, a modified expression of the Maxwell-Garnett formula exists. The DeltaPsi2 software can handle such cases where the shape is controlled by parameters Lx Ly and Lz, also called depolarization factors.

The following picture illustrates the corresponding software user interface.

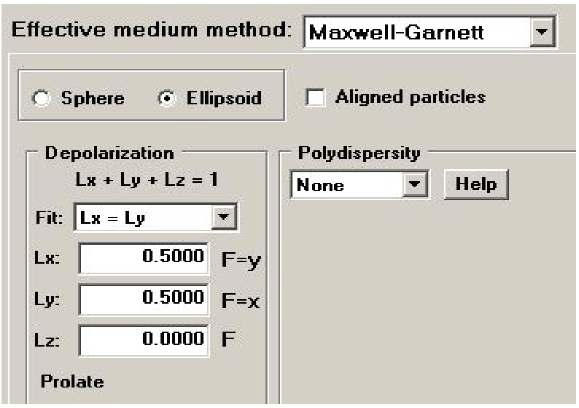

Figure 4: DeltaPsi2 user interface for modeling non spherical shapes of nanoparticles

We have applied this feature to characterize Ag nanowires. Nanowires can be approximated by nanospheres that are infinitely elongated along one direction. In the sample under study, 1% Ag nanowires were embedded into a polymer layer deposited onto a PET substrate. The next pictures illustrate the modeling results (fig 5a.) and the optical properties (fig 5b.) of the composite layer.

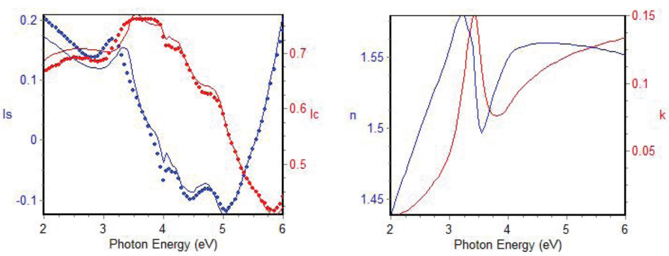

Fig 5a.: Ag Nanowire data and fit results - Fig 5b.: Optical index of the composite film

Generalization of Maxwell-Garnett for Shape Distribution

It is often likely that the chemical synthesis of nanoparticles will not produce perfectly monodisperse sizes or shape. Moreover, when the particles are in solution, they might often aggregate. Both effects, sources of imperfections in modeling, are illustrated below (fig 6).

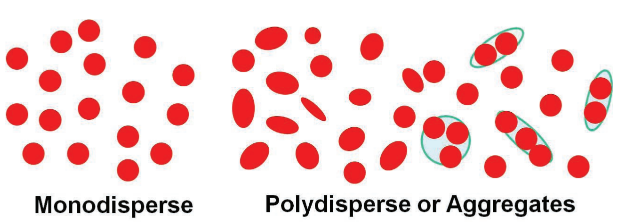

Figure 6: Illustration of dispersion in shape

There exists an extension of the Maxwell-Garnett theory available in DeltaPsi2 that can handle such non-idealities. We illustrate this effect in the next simulated pictures where we display extinction coefficients of 3 different gold nanoparticle aqueous solutions. These solutions are 10^{-3}% concentrated and the non-ideality is coming from different geometries of nanoparticles.

They are:
- 100% spherical nanoparticles (black)
- 100% nanorods (20% elongated spheres) (blue)
- A continuous distribution of shapes between the two previous cases (red)

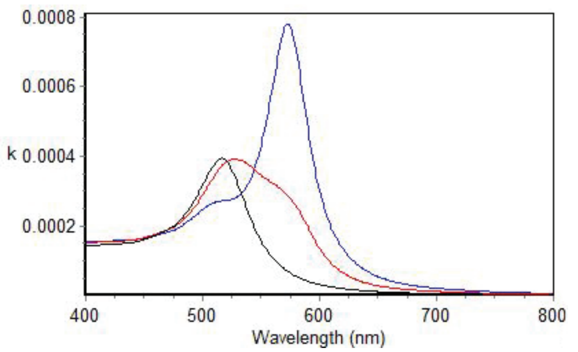

Figure 7: Extinction coefficient for Gold nanoparticle solutions. Spheres (black), Nanorods (blue), Mixture of spheres and nanorods (red)

From the above picture (fig 7) we can conclude that with DeltaPsi2 it becomes possible to qualitatively distinguish between:
- Spherical gold nanosphere solutions, with a characterictic sharp absorption peak near 520nm
- Monodisperse nanorod solutions with a split of absorption feature, characteristic for respectively transverse and longitudinal modes of absorption, the most intense being one at the highest wavelength
- A polydisperse mixture somehow intermediate with the two previous one, broadened and red shifted compared to the solution of pure spheres

2D Effects: Interaction Layer

The Maxwell-Garnett theory is typically a volume effect theory and cannot be applied in the 2D case of a monolayer of metallic nanoparticles deposited onto a non-conductive surface. In such case, under illumination, the nanoparticle acts like a dipole, as always, but when lying on a dielectric surface, it will modify the charge density of the surface. This phenomena, also called the mirror charge effect (fig 8) will result in an interfacial effect, showing vertical anisotropic polarization. This will induce anisotropic optical properties that can be detected when such a system is analyzed by ellipsometry.

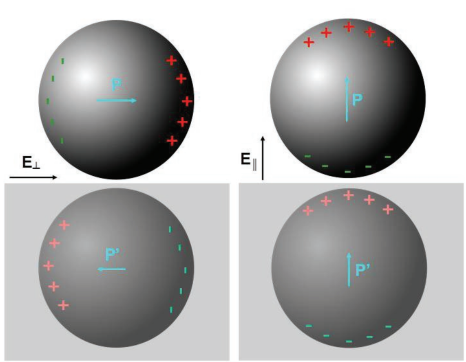

Figure 8: The mirror charge phenomena in a monolayer of nanoparticle under two different mode of electromagnetic external excitation, results in an anistropic polarization and anisotropic optical constants of the layer

DeltaPsi2 includes this feature of calculation, based on the Bedeaux and Vlieger theory, for spheroidal 2D coverage. The user interface and the effect of this interaction layer are illustrated below (fig 9a. and 9b.).

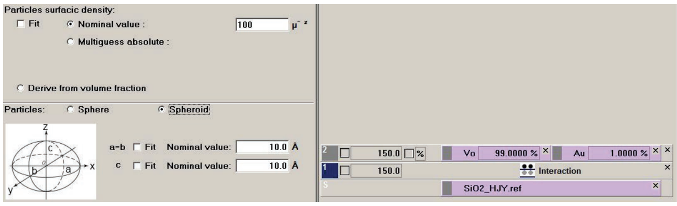

Fig 9a.: Interaction layer user interface

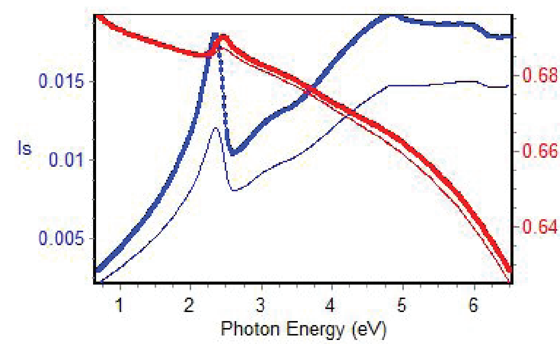

Fig 9b.: Ellipsometric simulations of 15nm Au nanoparticles deposited on SiO_2, with interaction layer activation (dots) and without interaction layer activation (solid line). Surface coverage was 100 particles μm^{-2} and density 1%.

Beyond Effective Medium Theories and, Towards Metamaterials

The examples illustrated above are compatible with the application of effective medium theories. As a reminder, this domain is restricted in terms of size of the nanoparticles, which should be small compared to wavelength of the probing light. Another restriction applies in the sense that no electromagnetic coupling between nanoparticles considered as plasmonic oscillators are taken into account. The breaking through of these limits is a possible definition for optical metamaterials. Indeed this new class of artificial materials can be seen as arrays of subwavelength plasmonic resonators. In such structures, according to the organization of the patterns, artificial magnetic permeability (μ) and optical activity (ξ, sometimes also called gyroscopic tensor) can be observed. Modeling such sytems is not possible with standard ellipsometric software where $\mu = 1$ and $\xi = 0$ and material properties are restricted to their dielectric tensor (ε).

The DeltaPsi2 software has been extended with these new magneto-optical tensors. The user interface for the magnetic one is illustrated below (fig 10.).

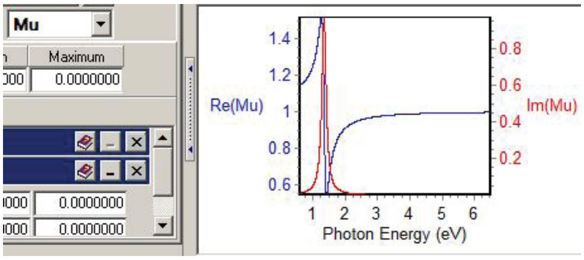

Figure 10: Illustration of dispersion for magnetic permeability. Similar interface exists for giroscopic tensor

The field of optical characterization for metamaterials is extremely wide and complex. The magneto-optical parametrization is intimately linked to the geometry of the resonators. We present here the application of the DeltaPsi2 metamaterials modeling feature to the specific case of a square array of U-shaped gold based oscillators obtained by electron beam lithography on ITO coated glass. A scanning electron picture of such a structure is illustrated next (fig 11.).

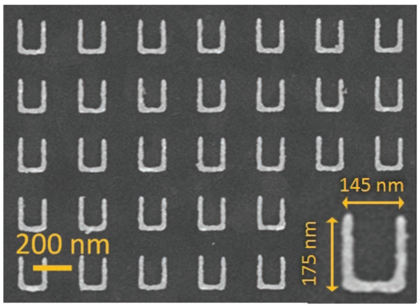

Figure 11: Picture of the array of gold split ring resonators

These samples being, strongly anisotropic, it is known that most information about them is generated by Mueller matrix measurements. An example of such acquisitions, accessible with a UVISEL phase modulated ellipsometer and corresponding modeling generated by Deltapsi2, are presented in the next picture (fig 12.).

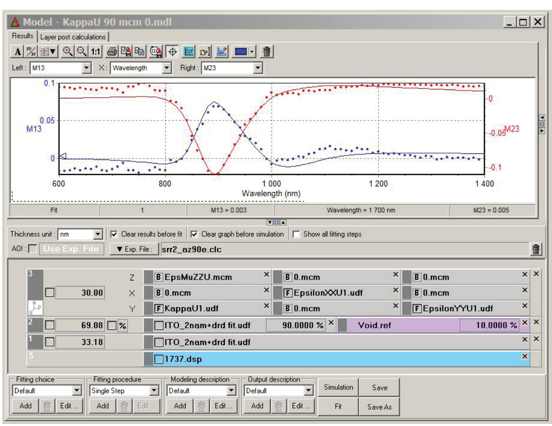

Figure 12: User interface illustrating Mueller Matrix modeling of metamaterial with DeltaPsi2

Conclusion

Through this report we illustrate the application of ellipsometry to the characterization of nanoparticle based samples. Our goal is to demonstrate that the technique can apply within a large panel of materials science. The HORIBA ellipsometric product line offers the most versatile hardware of the UVISEL series combined with the DeltaPsi2 software including unique modeling features to get the most of your applied work on this fascinating domain of modern physics.

Acknowledgements

HORIBA Scientific is grateful to the following scientists who contributed to the present work and agreed to its publication in this note.
Virginie Ponsinet, CRPP Bordeaux, France
Bruno Gallas, INSP Paris, France