Optical properties of silver nanoparticles embedded in dielectric films produced by dc and rf magnetron sputtering

G Tafur\textsuperscript{1}, C Benndorf\textsuperscript{2}, D Acosta\textsuperscript{3}, J Asencios\textsuperscript{2} and A Talledo\textsuperscript{2*}

\textsuperscript{1}Faculty of Industrial and Systems Engineering, Universidad Nacional de Ingeniería, Lima, Peru
\textsuperscript{2}Faculty of Sciences, Universidad Nacional de Ingeniería, Lima, Peru
\textsuperscript{3}Thin Film Laboratory, Instituto de Física, UNAM, Ciudad Universitaria, C.P. 04510, Mexico

*E-mail: atalledo@uni.edu.pe

Abstract. In this work it is reported the experimental production of silver-dielectric nanocomposites by the rf and dc magnetron sputtering techniques, as well as, the evolution of the plasmon resonance in silver nanoparticles as a function of the size of silver nanoparticles in the nanocomposites. Our nanocomposites are constituted by the intercalation of dielectric (Teflon, SiO\textsubscript{2}, TiO\textsubscript{2} or a-C) layers made by rf magnetron sputtering with layers of silver nanoparticles made by dc magnetron sputtering. Size of silver nanoparticles was modulated by changing the values of dc current of the plasma during deposition and keeping constant all the other parameters. High resolution transmission electron microscopy was used to observe the shape and size of nanoparticles. The chemical composition and crystalline structure of the materials were analyzed by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. UV-visible spectroscopy in the 350-1100 nm range was used to study the plasmon-resonance evolution. Dipolar and Quadrupolar Plasmon resonance were observed and interpreted in terms of the Mie theory.

1. Introduction
Silver nanoparticles embedded in dielectric films have been widely investigated in the last two decades due to the technological interest they arouse in different areas of the knowledge. For example, silver nanoparticles embedded in TiO\textsubscript{2} and Teflon have been investigated for their antibacterial properties [1,2]. Also, silver nanoparticles immerse in dielectrics as SiN\textsubscript{x} and SiO\textsubscript{2} are recently strongly investigated for their applications in so called plasmonic solar cells [3,4]. In this paper we concentrate ourselves in the optical properties of silver nanoparticles embedded in Teflon, TiO\textsubscript{2}, SiO\textsubscript{2} and a-C. The main feature of spectral optical absorption of metal particles inserted in dielectric materials is a strong absorption in a determined wavelength value or a range of wavelength values. This feature has been explained since 1908 by Mie [5] and afterward in advanced books on electromagnetism [6]. A good reference to understand the properties of metal clusters is the very specialized book by Kreibig and Vollmer [7]. In the present decade, it is most common refer to this absorption as surface plasmonic resonance because absorption is related to collective oscillations of free electrons in a metal at well-
defined frequencies which can be quantized. In the Mie theory, the interaction between a plane electromagnetic wave and a sphere of radius $R$ with complex dielectric permittivity surrounded by an infinite medium of real dielectric permittivity is studied. The incident plane wave is expressed as a multipolar expansion; boundary conditions allow us to calculate scattered and absorbed radiation. From this data it is possible to simulate an absorptance spectrum for each size of metal particle. In this paper, we produced silver nanoparticles embedded in four different media, we made the optical measurements of transmittance and, neglecting scattering, we obtain the spectral absorptance $A = 1 - T$. We compared then our experimental results with those of Mie theory. The neglecting-scattering approximation is valid when the radius of silver nanoparticles is much less than the wavelength of incident radiation.

2. Experimental

Nanocomposites silver/dielectric were produced by intercalating layers of silver nanoparticles produced by dc magnetron sputtering and thin films of transparent dielectrics (Teflon, SiO$_2$, TiO$_2$ and a-C) produced by rf magnetron sputtering. The structure is schematically shown in Figure 1. In order to obtain silver nanoparticles of different sizes, all the deposition parameters were kept constant, except the sputter current $I$, which took values of 100, 200, 300 and 400 mA. The deposition time was chosen to be 8 seconds for each layer of nanoparticles. The oxide films were produced by reactive sputtering of Ti and Si targets of 99.9 % purity in an atmosphere of 8% O$_2$ + 92% Ar. Teflon and a-C films were produced by sputtering white Teflon and graphite disks, respectively, in an atmosphere of Ar 99.999% purity. The size of the targets was always 76.2 mm diameter and 4 mm thick. The base pressure was $10^6$ mbar and the deposition pressure was $5 \times 10^{-3}$ mbar. The rf-power was 60 W and the deposition time for dielectric layers was 10 min, except for graphite which was only 6 min.

![Figure 1](image_url). Schematic of nanocomposites silver/dielectric produced by dc and rf magnetron sputtering.

Some of our samples were observed by high resolution transmission electron microscopy (HRTEM) in order to determine shape and size of silver nanoparticles. Chemical composition of our nanocomposites was analyzed by X-ray photoelectron spectroscopy (XPS), crystalline structure was studied by X-ray diffraction. Optical transmittance of each system ($T$) was measured in the range 300-1100 nm wavelength range and from the spectral transmittance we obtained the absorptance $A$ by the formula (1).

$$A = 1 - T$$ (1)

HRTEM micrographs were taken by using the instrument JEM-4000E which was operated at 400 keV, the maximum resolution was 0.17 nm. We only obtained HRTEM micrographs for the samples with structure Teflon/Ag/Teflon/Ag/Teflon, where the dc current for silver deposition was 100 mA and the deposition time for Teflon films was 10 minutes at a power of 60 W. The films were extracted from the substrate using an ultrasound equipment. After 15 minutes, fragments of the films floating in the water were obtained; one of these fragments was “fished”, placed on a grid and introduced to the sample holder of the instrument. X-ray photoelectron spectroscopy was carried out by using the system ESCA/SAM PHI Model 550 with source of radiation Al K-alpha of 1486.6 eV. X-ray diffraction was carried out by using the instrument Bruker D8 Advance with theta-2theta configuration by using X-ray
from a cooper anode with wavelength = 0.154 nm. Optical transmittance in the wavelength range from 350 to 1100 nm was carried out in a UV Visible Shimadzu Spectrophotometer model 1240.

3. Results and discussion

We divide this section in two subsections: In subsection 3.1 we show the results of general characterization, i.e., morphology obtained by HRTEM, chemical composition determined by XPS and crystalline structure of silver nanoparticles achieved by XRD. In subsection 3.2 we present the results of optical measurements, we discuss them in terms of Mie theory and compare them with previous results obtained by other authors we have found in the literature.

3.1 General Characterization

In Figure 2(a) we show a micrograph where it can be seen the size and shape of silver nanoparticles embedded in Teflon. They are spheroidal shaped and the size is variable with an average diameter of 20 nm. In Figure 2(b), with better resolution, we can see some families of crystalline planes constituting the silver nanoparticles. From this information the fcc structure with lattice parameter with a = 0.408 nm was confirmed.

![Figure 2](image.png)

**Figure 2.** (a) HRTEM micrograph which allows us to see the shape and determine de size of silver nanoparticle embedded in Teflon. (b) HRTEM which allows us to determine the crystalline structure of silver nanoparticles embedded in Teflon.

In Figure 3(a) we show an XPS spectrum between 0 and 1000 eV for one sample of silver nanoparticles embedded in TiO$_2$ made by dc and rf magnetron sputtering according with structure shown in Figure 1. With help of the manual of the instrument [9] we identified intensity peaks of electrons coming from atoms of titanium, oxygen and silver, as expected. Intensity peaks of electrons from titanium atoms show binding energy at 30 eV and 60 eV corresponding to Ti(3p) and Ti(3s) respectively; we can see also a doublet close to 460 eV corresponding to Ti(2p) electrons; there is other peak clearly defined at 560 eV which is attributed to Ti (2s) electrons. In the energy interval between 800 and 900 eV it is observed the characteristic Auger spectrum for Ti(LMM). The peak observed at 530 eV corresponds to O(1s) electrons. The intensity peak corresponding to electrons from silver nanoparticles is located for binding energy values between 360 and 370 eV and it corresponds to Ag(3d) electrons. In Figure 3b a detailed XPS spectrum for binding energies between 360 and 380 eV is shown and we can appreciate that the electrons from silver nanoparticles actually come from a doublet at 369.2 and 375.3 corresponding to Ag 3d$_{5/2}$ and 3d$_{3/2}$ quantum states. Similar XPS spectra and similar analysis were made, but the results
lies beyond the scope of this paper, for silver nanoparticles embedded in other dielectric: Teflon, SiO$_2$ and a-C.

![Figure 3](image_url)

**Figure 3.** (a) General XPS spectrum for a sample of silver nanoparticles embedded in TiO$_2$. (b) Details of the XPS spectrum in the range 360-380 eV which allows to determine the quantum state of silver atoms in nanoparticles. The position of the peaks vary slightly when TiO$_2$ is replaced by SiO$_2$, a-C or Teflon.

In Figure 4 we show X-ray diffractograms for silver nanoparticles embedded in TiO$_2$. Diffractogram in Figure 4(a) corresponds to silver nanoparticles produced at sputter current I = 200 mA and diffractogram in Figure 4(b), I = 400 mA. The main feature of these diffractograms is the presence of diffraction peaks at angle values: $2\theta = 38.2^\circ$, 44.4$^\circ$, 64.6$^\circ$ and 77.6$^\circ$ corresponding to crystalline-plane families [111], [200], [220] and [311] respectively. The positions of these diffraction peaks agree with the fcc structure a = 0.408 nm for metallic silver [10] and with the structure obtained before in this paper by HRTEM.

![Figure 4](image_url)

**Figure 4.** X-ray diffractograms for samples of silver nanoparticles embedded in TiO$_2$ with silver nanoparticles sputtered with current (a) I = 200 mA and (b) I = 400 mA.

The better resolution of diffraction peaks in Figure 4(b) indicates a greater grain size, in accordance with Sherrer formula [11]:

$$D = \frac{K \lambda}{\beta \cos \theta}$$  

(2)
By using eq. (2), it is calculated for $I = 200 \ mA$, $D = 2R = 12 \ nm$ and for $I = 400 \ mA$, $D = 2 \ R = 80 \ nm$. It is evident that size of nanoparticles increases with sputter current ($I$).

3.2 Optical measurements and Mie Theory

We start this subsection by showing the absorption spectra of silver nanoparticles embedded in four different kinds of transparent dielectrics, Teflon, titanium dioxide, silicon dioxide and amorphous carbon. We include in each figure the absorptance spectrum of a dielectric film without silver nanoparticles ($I = 0 \ mA$).

![Figure 5](image)

**Figure 5.** Optical absorptance spectra of: (a) one thin film of Teflon and three samples of Ag nanoparticles embedded on Teflon, (b) one thin film of SiO$_2$ and three samples of Ag nanoparticles embedded in SiO$_2$, (c) one thin film of TiO$_2$ and three samples of Ag nanoparticles embedded in TiO$_2$, (d) one thin film of a-C and three samples of Ag nanoparticles embedded in a-C.

In the Mie theory, electromagnetic plane waves of incident radiation are expressed as a series of multipolar terms in spherical coordinates; metallic spheres of radius $R$ are characterized by a complex dielectric permittivity: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$; $\varepsilon_m$ is the real dielectric permittivity of the
transparent dielectric medium surrounding the silver nanoparticles. Boundary conditions allow to
calculate extinction and scattering electromagnetic fields of each multipolar term and then the respective
cross sections which are the quantities to compare with experimental data [7].

\[
\sigma_{\text{ext}} = \frac{\lambda^2}{2\pi} \sum_{L=1}^{\infty} (2L+1) \left[ \text{Re} \{a_L + b_L\} \right] 
\]

\[
\sigma_{\text{scat}} = \frac{\lambda^2}{2\pi} \sum_{L=1}^{\infty} (2L+1) \left[ |a_L|^2 + |b_L|^2 \right] 
\]

\[
\sigma_{\text{abs}} = \sigma_{\text{ext}} - \sigma_{\text{scat}} 
\]

In equations (3) and (4), subscript \(L=1\) means dipolar term, \(L=2\) quadrupolar term, \(L=3\) octupolar term
and so on. Terms \(a_L\) and \(b_L\) are calculated from boundary conditions and they are proportional to
\(|R/\lambda|^L\) and \(|R/\lambda|^{2L}\), respectively. It is clear from equations (3) and (4) that if \(R << \lambda\), then \(\sigma_{\text{abs}} \approx \sigma_{\text{ext}}\). The most important terms in the series (3) and (4) are those for \(L=1\), i.e., dipolar resonance. From this, it is deduced:

\[
\sigma_{\text{abs}}^{\text{dip}} \approx \sigma_{\text{ext}}^{\text{dip}} = 9\omega^3 c \varepsilon_0 \varepsilon_m^{3/2} V_0 \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + [\varepsilon_2(\omega)]^2} 
\]

where \(V_0\) (proportional to \(R^3\)) is the volume of the particle. Dipolar resonances occur when the
denominator is minimum. If \# is the number of particles per area unit then \# \(\sigma_{\text{abs}}(\omega)\) is directly related
to the absorbance \(A\). Thus, maxima of equation (6) should predict absorption peaks in spectral
absorptance, however, the situation is complicated because the dielectric permittivity of metal
nanoparticles depend strongly on their size. A useful approximation valid for \(\omega >> \Gamma\) is:

\[
\omega_1 = \omega_p \frac{1}{\sqrt{1 + 2\varepsilon_m}} 
\]

for dipolar resonances and

\[
\omega_1 = \omega_p \frac{1}{\sqrt{1 + \frac{L+1}{L} \varepsilon_m}} 
\]

for higher multipole resonances, where \(\Gamma\) denotes the phenomenological damping constant for electrons
in the metallic nanoparticles; in the Drude Model, it coincides with the inverse of the electron relaxation
time \(\tau^{-1}\).
By using size dependent dielectric functions, Berg et al. [8] gives a compilation of results of the Mie theory in a graphic form which results a comparison guide for experimental results of spectral absorbance. This information is also available in page 84 of reference [7]. According with this, the position of the photon energy for dipole resonances of silver nanoparticles decreases monotonically with size between $2R = 15$ nm and $2R = 50$ nm, i.e., there is a red shift of dipole resonances when $R$ increases. Also, there is a more noticeable red shift if for a constant size of the nanoparticle, the electrical permittivity of the surrounding medium increases.

Table 1. Position and halfwidth of dipolar resonances in silver nanoparticles embedded in Teflon as a function of sputter current ($\varepsilon_m=1.8$).

| Sputter current I (mA) | Estimated diameter of nanoparticles (nm) | Photon Energy (eV) | Halfwidth (eV) |
|----------------------|----------------------------------------|-------------------|---------------|
| 100                  | 20                                     | 2.81              | 0.48          |
| 200                  | 40                                     | 2.50              | 0.78          |
| 300                  | 60                                     | 2.45              | 1.29          |
| 400                  | 80                                     | 2.21              | -             |

Table 2. Position and halfwidth of dipolar resonances in silver nanoparticles embedded in silicon dioxide as a function of sputter current ($\varepsilon_m=2.2$).

| Sputter current I (mA) | Estimated diameter of nanoparticles (nm) | Photon Energy (eV) | Halfwidth (eV) |
|----------------------|----------------------------------------|-------------------|---------------|
| 100                  | 20                                     | 2.53              | 1.27          |
| 200                  | 40                                     | 2.40              | 1.89          |
| 300                  | 60                                     | 2.31              | 2.08          |
| 400                  | 80                                     | 2.06              | -             |

Table 3. Position and halfwidth for dipolar resonances in silver nanoparticles embedded in titanium dioxide as a function of sputter current ($\varepsilon_m=6.2$).

| Sputter current I (mA) | Estimated diameter of nanoparticles (nm) | Photon Energy (eV) | Halfwidth (eV) |
|----------------------|----------------------------------------|-------------------|---------------|
| 100                  | 20                                     | 2.81              | 0.48          |
| 200                  | 40                                     | 2.69              | 0.78          |
| 300                  | 60                                     | 2.52              | 1.29          |
| 400                  | 80                                     | -                 | -             |

Most of the resonances observed in our absorption data can be explained as dipolar resonance, except one absorption peak in Figure 5a, at photon energy 3.09 eV and one in Figure 5b, at photon energy 3.34 eV, which we attribute to quadrupole resonances of silver nanoparticles embedded in Teflon and silicon dioxide respectively. These results are similar to those reported by Russell et al. [12]. In Tables 1, 2 and 3 we summarize the position and halfwidth of resonance peaks due to nanoparticles embedded in three dielectrics: Teflon, SiO$_2$ and TiO$_2$. In all cases we observe a redshift with increasing the value of the plasma current during sputter deposition. It is also noticeable that the halfwidth of the absorption bands increases with the intensity of deposition current. This agrees with the information given by Berg et al. [8] and Kreibig [7] about the dipolar resonances when the size of the silver nanoparticles increases. The
halfwidth of resonance peaks is especially large for silver nanoparticles embedded in titanium dioxide whose dielectric permittivity is very high relative to Teflon and SiO$_2$; however, we do not observe a special large redshift in TiO$_2$ due to the high value of dielectric permittivity, as suggested in references [7] and [8]. We observe that silver nanoparticles embedded in amorphous carbon do not follow the same features as in other here-studied media. One explanation could be that even previous to the silver deposition graphite in amorphous carbon presents already certain absorption (20%) and what is observed with the insertion of nanoparticles may only be a broadening of this absorption.

4. Conclusions
It has been proved, with this work, that it is possible to produce systems of metal nanoparticles embedded in dielectric films by magnetron sputtering techniques and that it is possible to modify the size of the nanoparticles by varying the intensity of deposition current. The evolution of absorption peaks for silver nanoparticles embedded in Teflon, SiO$_2$ and TiO$_2$ reported in this work are very well explained by Mie theory: Position of dipolar resonances moves toward larger wavelengths and halfwidth increases when the size of nanoparticles increases. For sizes larger than 60 nm quadrupolar Mie resonances were observed.

Acknowledgments
One of us, J.A., is very grateful to CONCYTEC for a scholarship financing doctoral studies. A.T. is also very grateful to Universidad Nacional de Ingeniería and MINEDU Perú for special grants as a researcher professor. We are very thankful to H. Huanca and C. Luyo for achieving our X-ray diffractograms.

References
[1] Schürmann U, Hartung W, Takele H, Zaporotchenko V and Faupel F 2005 Nanotechnology 16 (8) 1078-82
[2] Sun S-Q, Sun B, Zhang W and Wang D 2008 Bull. Mater. Sci. 31, 61-66
[3] Babonneau D, Lantiat D, Camelio S, Toudert J, Simonot L 2008 Eur. Phys. J. Appl. Phys. 44 3-9
[4] Atwater H A and Polman A 2010 Nature Materials 9 205-13
[5] Mie G 1908 Ann. Phys. 25 377-445
[6] Stratton J A 1941 Electromagnetic Theory McGraw-Hill Book Company New York and London pp 563-570
[7] Kreibig U and Vollmer U 1995 Optical Properties of Metal Clusters Springer Series in Materilas Science 25 Springer Verlag Berlin-Heidelberg pp 13-202
[8] Berg K-J, Berger A and Hofmeister H 1991 Z. Phys. D 20, 309-311
[9] Moulder J F et al. 1992 Handbook of X-ray Photoelectron Spectroscopy Perkin-Elmer Corporation Minnesota USA pp 72-121
[10] Kittel C 2005 Introduction to Solid State Physics John Wiley and Sons, Inc 8th edition New Jersey USA p 20
[11] Scherrer P 1918 Nachrichten von der Gesellschaft der Wissenschaften Goettingen Mathematische-Physikalische Klasse 2 98-100
[12] Russell B K, Mantoyani J G, Anderson V E, Warmack R J and Ferrell T L 1987 Physical Review B 35 2151-4