

Effect of post-annealing on structural and optical properties of gold nanoparticles embedded in silica films grown by RF- sputtering

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Abstract

Gold-Silica nanocomposite thin films were prepared by RF-magnetron sputtering technique on glass substrate at room temperature. Subsequent thermal treatment was used to promote nanocluster formation. The prepared samples were characterized by X-ray diffraction and optical absorption spectroscopy. After annealing, an increase of size accompanied by an increase of the lattice constant parameter is observed. A value of the surface stress coefficient of gold is $f = 3.20 \text{ N/m}$ has been obtained. Broad band absorption, with maximum absorbance at around 500 nm, characteristic of gold nanoclusters was observed after heat treatment. Experimental optical absorption spectra were modeled by the modified Mie theory. The plasmon peak red shift obtained from the simulation curves is compared to the calculated one from the variation of lattice constant parameter.

Keywords: Au nanoparticles, silica films, X-ray diffraction, surface plasmon résonance, lattice contraction.

1. Introduction

It is well known that metallic nanoparticles have various unusual chemical and physical properties compared with those of metal atoms or bulk metal. They are of great interest because they open a new field in fundamental science and because their potential technological and biomedical applications. For these applications, the ability to modify and control the size of the metal is of a great importance. Noble metal, particularly gold and silver display unique optical properties. When they interact with an electric field, a very strong absorption is observed called the surface plasmon resonance (SPR) [1, 2], resulting from the collective oscillation of the electrons in conduction band from one surface to another of the particle. This oscillation has a frequency that absorbs the visible light, when the frequency of electromagnetic field becomes resonant with the coherent electron motion. The spectral position of the SPR in the compound materials can be designed within a wide spectral range covering the visible and near-infrared spectra by a choice of electronic properties of the metal and the dielectric matrix, or by manipulating the particle size, shape, inter-particle separation [1-6]. The SPR was first quantitatively described by Mie [7] by solving Maxwell's equation with the appropriate boundary conditions for spherical particles. The solution was obtained with the assumption that all the spheres are of the same diameter and the relative separation distances are large such that no interaction between the different scatters needs to be taken into account.

For nanoparticles much smaller than the wavelength of the absorbing light, only the dipole oscillation contributes significantly to the extinction cross section and thus Mie's theory is reduced to the following equation [7]:

$$\sigma_{abs} = \frac{3}{2} \frac{\omega}{c} \varepsilon_m^{3/2} \pi D^3 \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2^2(\omega)} \quad (1)$$

Where D is the spherical particle diameter, c the speed of light in the vacuum, ω is the angular frequency of the exciting radiation, ε_m is the dielectric constant of the surrounding medium (assumed to be frequency independent). $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ denote the real and imaginary part of the dielectric function of the particle material, respectively. A resonance in the spectrum of σ_{abs} will occur whenever $\varepsilon_1(\omega) = -2\varepsilon_m$. According to Equation (1), the

plasmon absorption is size-independent within the dipole approximation. However, experimentally a size dependence of the surface plasmon absorption was early observed with decreasing of particle size. Contradicted with experimental observations, Mie's theory has evolved to include the fundamental assumption, that the dielectric function of the nanoparticle material is size dependent, when particle size becomes of the order of the mean free path of the conduction electrons, or even smaller. A size dependence for the quasi-static regime is introduced in equation (1) by assuming a size-dependent material dielectric constant $\varepsilon(\omega, D)$ [8]:

$$\varepsilon(\omega, D) = \varepsilon_{bulk}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\Gamma_{bulk}} - \frac{\omega_p^2}{\omega^2 + i\omega(\Gamma_{bulk} + 2Av_F/D)} \quad (2)$$

Where $\varepsilon_{bulk}(\omega)$, ω_p , v_F and Γ_{bulk} being, the dielectric function, the plasmon frequency, the Fermi velocity and the damping constant of the bulk metal respectively, and A is a phenomenological parameter including details of the scattering process. The modified Mie theory succeeds in terms of spectra of relatively large particles (> 3 nm for gold) but does not agree with the experimental results when applied to the smaller sizes. It was found that the plasmon band is strongly damped and even disappears completely where size is less than about 2 nm [9].

Several techniques, such as RF magnetron sputtering [10], ion implantation [11] and sol-gel synthesis [12] have been used to introduce gold into dielectric matrices. Among these techniques, RF-Sputtering is chosen due to its relative simplicity, growth of large area films and flexibility concerning choice of material combinations.

In this work, Au/SiO₂ nanocomposite films were synthesized on glass substrate at room temperature by RF-magnetron sputtering technique. The as-deposited and heat-treated films were characterized by X-ray diffraction and optical absorption spectroscopy. Evolution of structural and optical properties of gold nanoparticles in silica matrix as a function of temperature has been studied. The subsequent annealing allows one to follow the change of the SPR band absorption around the critical size of gold nanoparticles.

2. Experimental methods

Au/SiO₂ nanocomposite films were prepared using an Alcatel SCM 650 RF-magnetron sputtering system, in an argon atmosphere, on glass substrates (ISO 8037). The target consisted of pure metal Au chips on top of a 50 mm diameter silica disc placed 60 mm away from the substrates. The RF power and deposition pressure were fixed at 50W and 5.10⁻³ mbar respectively, during the sputtering process. The films were deposited at room temperature for 4h30 min. Sputter deposition, in a radio-frequency (13.56 MHz) machine, has been carried out after the chamber reached a base pressure better than 1.10⁻⁶ mbar. The prepared samples were annealed at different temperatures for 1hour each.

The structural characterization of the composite films were performed in a Philips PW 1710 spectrometer using Cu K_α radiation $\lambda = 1.5418 \text{ \AA}$. The diffraction patterns were collected over the range $2\theta = 10^\circ$ to 80° at room temperature.

Optical absorption spectra, of Au/SiO₂ composite films, were registered by a Shimadzu UV 30101 PC spectrometer, in near ultra-violet-visible-near infra-red range (NIV-VIS-NIR) from 300 to 2000 nm

3. Results and discussions

3.1 Structural analysis

Fig.1 shows the XRD pattern for Au/SiO₂ composite film deposited at room temperature under 5.10⁻³ mbar Ar pressure. The spectra of the sample don't reveal clearly diffraction peaks corresponding to Au or the silica material, but exhibits a shoulder in the range 35°- 47°, and a broad peak at $2\theta=64^\circ$. Fig.2 (a and b) show the XRD patterns of gold and Au/SiO₂ composite thin films. The gold thin film spectra taking as a reference, exhibits three diffraction peaks, which may be assigned to crystalline gold cubic phase according to JCPDS (n° 04-0784). The three diffraction peaks corresponding to the (111), (200) and (220) gold planes appear at 2θ positions 38.18°, 44.39° and 64.58° respectively. It can be expected that the spectra of the composite film reported in Fig.1, results from the superposition of two diffractograms, assigned to small gold particles and the amorphous silica matrix.

The crystalline phases of the Au/SiO₂ composite film were determined from a deconvolution procedure of the XRD spectrum, with commercial software (program) available on our computer. Note that the purpose of the

deconvolution is to fit the measured XRD spectrum in well-defined peaks to which a physical meaning can be attributed. For more details see reference [13]. Fig.3 shows the experimental diffractogram and their curve fitting of the Au/SiO₂ composite sample deposited at room temperature. Therefore, the XRD spectra of the composite film have to be deconvoluted with four peaks as illustrated in Fig.3. The peak centered around 2θ=26° corresponds to the amorphous silica. The comparison of the three peaks with a JCPDS database are attributed to (111), (200), and (220) reflections of the Fcc structure of Au nanocrystals. The peaks are considerably broadened; the extent of broadening is described by full width at half maximum intensity of the peak (FWHM). This broadening of the diffraction peak is related to the size nanoparticle D via the Scherrer's formula:

$$D = \frac{0.9\lambda}{(FWHM)\cos\theta_B} \quad (3)$$

Where λ is the X-ray wavelength and θ_B is the Bragg angle of the peak. On the basis of the peak width (FWHM) in radians at a 2θ value, we calculated the particle size D using the Equation (3). From Bragg equation: 2dsinθ = λ, where $\mathbf{d} = \mathbf{a}/(\mathbf{h}^2 + \mathbf{k}^2 + \mathbf{l}^2)^{1/2}$, the lattice constant for gold particles in the films can be calculated. The parameters obtained from the XRD spectra for the as-grown Au/SiO₂ film are listed in the Table1. The estimated particle size is 0.90 nm corresponding to the Au (111) peak. For other peaks, it takes 0.6 nm and 0.8 nm for (200) and (220) reflections respectively. The lattice parameter of gold particles determined from the Au (111) reflections equals to 4.035 Å, is smaller than 4.0786 Å of that given in JCPDS (n° 04-0784), there seems to be a lattice contraction.

XRD spectra for Au/SiO₂ nanocomposite films annealed at various temperatures are presented in Fig.4. Characteristic peaks representing pure Au were not very prominent in all the samples and no peak corresponding to SiO₂ was observed, indicating that after annealing process, there is no crystallized SiO₂ in these films.

The results of the deconvolution of the XRD spectrum of the composite films as-grown and annealed at different temperatures are reported in Table (2). The particle size, which was calculated from the Au (111) diffraction peak according to Scherrer formula, varied from 0.9 nm to 1.5 nm, and the lattice constant parameter increased when heat-temperature varies from 25°C to 500°C. So, lattice contraction depends implicitly on the particle size. These experimental data are used to deduce the surface stress coefficient of Au particles. In the case of spherical particles with a cubic structure, it has been shown [14] that the change in lattice parameter Δa is proportional to the reciprocal of the particle size:

$$\frac{\Delta a}{a_0} = -\frac{4kf}{3D} \quad (4)$$

where f is the surface or interface stress, a₀ is the lattice constant and k is the compressibility of the bulk material. Therefore, a measure of the lattice variation parameter Δa allows us to determine the surface stress f.

The graphical representation of the lattice spacing versus the reciprocal diameter of Au is shown in Fig.5. So, from the slope of the linear regression, the interface stress is evaluated according to the equation (4), with the value for the compressibility of bulk gold, K = -5.99x 10⁻¹² m² N⁻¹ [14]. The value of f = 3.20 N/m has been obtained for Gold clusters embedded in a silica. A comparison to published experimental f coefficients shows that the determined surface stress coefficient is lower than, f = 3.83 N/m, determined by Solliard and al [15], and in good agreement with, f = 3.32 N/m, measured by Umeno et al [16].

3.2 Optical absorption

The optical absorption spectra for the as-deposited and for the various heat-treated nanocomposite films are shown in Fig.6. For the as deposited sample, the SPR peak characteristic of the gold particles is not discernable. The nonappearance of an absorption peak in the unannealed sample can be associated to the gold particle sizes smaller than 2 nm [17]. With the increase of annealing temperature, a progressive of a broad band appears. The optical absorption bands of all samples are very broads and it is very difficult to assign a definite value of a wavelength of maximum absorption. So, the measured optical absorption curves were modeled based on Mie theory taking into account the mean free path of gold bulk conduction electrons. The size effect was considered applying Equations (1 and 2). The values of the plasma frequency ω_p = 1.39x10¹⁶Hz, the dielectric constant values of the matrix

$\epsilon_m \approx 2.16$ and the gold bulk has been taken from [18]. The best fit is obtained with 1.4 value attributed to the parameter A [8]. The simulation and the experimental plots are shown in Fig.7. These fitting allowed us to evaluate, the gold particle size, the wavelength λ_{max} of the SPR band absorption spectra. The plasmon peak positions just vary from 500 nm to 505 nm, and the size increases slightly from 2.1 nm to 2.3 nm when heating temperature from 300 to 500°C. The Au sizes estimated from optical absorption spectra are larger than those measured from XRD. It is probably due to that the Scherrer equation is based on size limited bulk structure and relating particle size to the peak width, cannot be used with great accuracy for very small clusters [19].

It can be noted here, that the optical properties are more sensitive to the aggregation of gold growth than XRD measurements. The changes occurring in the Au nanocrystals upon increasing temperature show, when the gold particle size exceed slightly the well known critical size (≈ 2 nm), superimposed on the background, a broad surface plasmon band around 500 nm occurs characteristic of gold nanoclusters, due to surface plasmon resonance. This absorption band is consistent with the reported value for gold nanoparticles, where SPR appears around 500 nm [20-24]. Similar observations have been reported for other gold-dispersed dielectric materials: Alvarez et al [17] prepared passivated gold particles with sizes in the range 1.4-3.2 nm, found that with decreasing size, the SPR band broadened until it became unidentifiable for sizes less than 2 nm. Palpant et al [20] found also, that the plasmon absorption is damped and blueshifted with decreasing particle size, in the case of gold clusters in the size range 2-4 nm, embedded in alumina matrix grown by co-deposition technique using pulsed laser ablation.

Lastly, we have studied the heating effect on gold nanoparticles embedded in silica films. A blueshift and broadening of the resonance with decreasing particle size was observed. It was found also that lattice contraction increases with the decrease of particle size. This lattice contraction induced by surface stress has an impact on the optical properties of very small metallic nanoparticles, has been studied by several authors [25-27]. In this work, the Mie resonance frequency was calculated exploiting the lattice constant variation estimated from the XRD measurements, based on the equation (10) from the reference [28]:

$$\omega_s = \frac{\omega_p(\infty) \left(1 - \frac{3 \Delta a}{2 a_0} \right)}{\sqrt{\epsilon'_d(\omega_s) + 2\epsilon_m}} \quad (5)$$

Where ϵ'_d is the real component of the core electron dielectric function. The core electrons have an important influence on the Mie frequency. Taking $\epsilon'_d = 1 - \frac{9}{\epsilon_0^2} \frac{1}{D^2}$, independent of size D, the maximum wavelength calculated from the Equation(5) is found in the range 500 – 508 nm, when annealing temperature varies from 25°C to 500°C. The values obtained are comparable to those estimated from the simulation of the optical absorption curves. Consequently, the effects of lattice expansion on both the free-electron response and core response, plays an important role in determining the resonant energy as reported in the works[27, 29], is probably one of the origin of the slight redshift observed.

4. Conclusion

The post-annealing effect on the structural and optical properties of the gold nanoparticles dispersed in silica films grown by RF-magnetron sputtering was studied. The presence of small gold nanoclusters with size below 2 nm inside the silica matrix was confirmed by XRD and optical absorption measurements in the as deposited samples. After annealing, the size and lattice constant parameter of gold nanoparticles increase. According to modified Mie theory, the plasmon band of gold clusters shifts from 500 nm to 505 nm. The simulation results are consistent with the redshift calculated from the lattice variation parameter. These experimental results show the ability to create and control very small gold clusters inside dielectric films, by a combination of the sputtering deposition parameters and subsequent heat-treatment.

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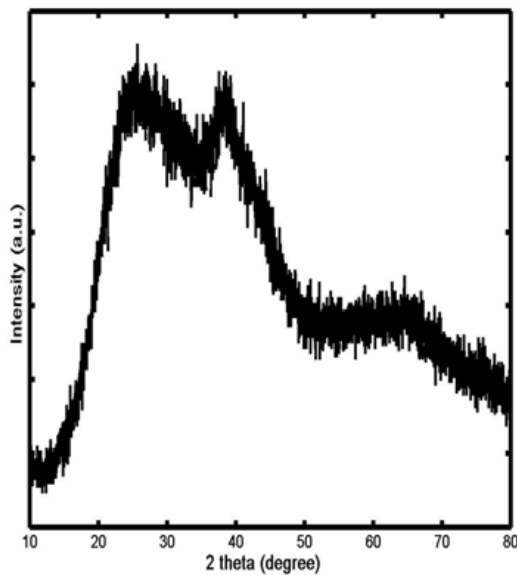


Figure 1 : XRD spectra of Au/SiO₂ composite deposited under 5.10⁻³ mbar argon pressure at room temperature

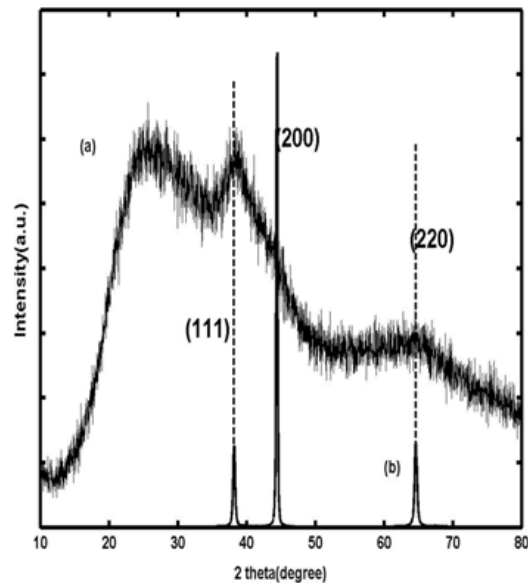


Figure 2: XRD diffractograms of Au/SiO₂ nanocomposite and gold thin films

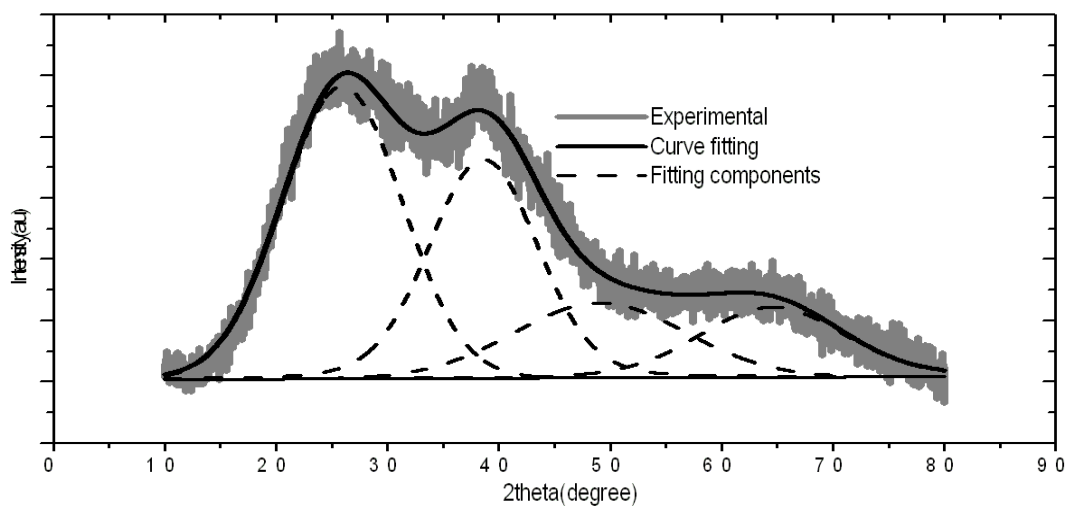


Figure 1: XRD diffraction patterns of as –deposited sample and their curve fitting

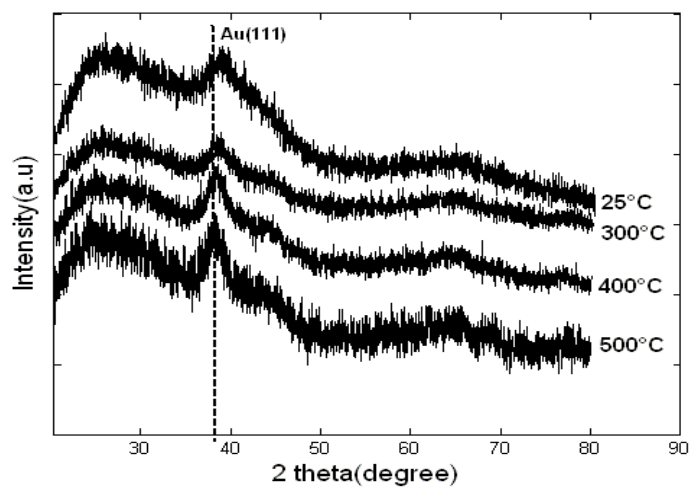


Figure 4 : XRD spectra of Au/SiO₂ nanocomposite thin films as-deposited and after heated at 300°C, 400°C and 500°C

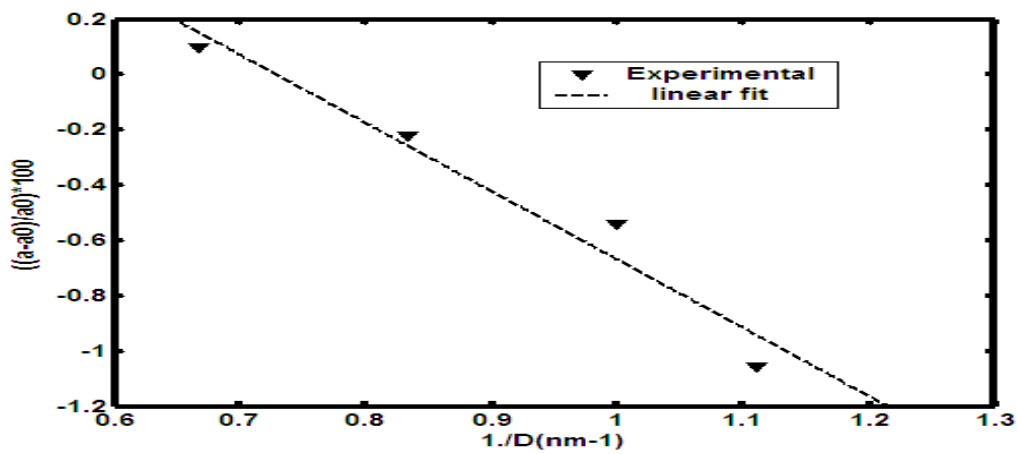


Figure 5: variation of the relative lattice parameter $\Delta a/a_0$ as a function of the reciprocal diameter of Au particles embedded in silica matrix. The line represents linear fit to the simulation data

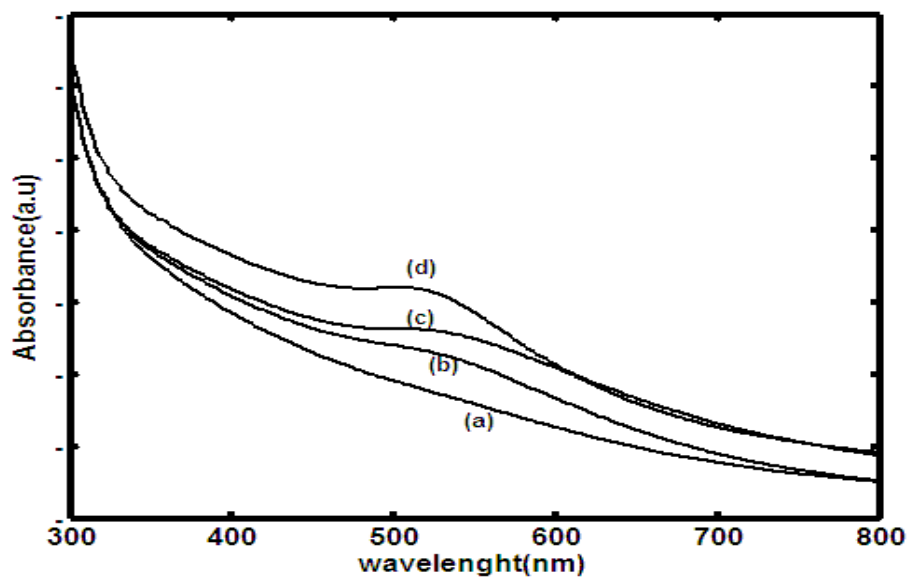


Figure 6: Optical absorption spectra of Au/SiO₂ thin films : (a) as-deposited and different annealing temperatures: (b)300°C, (c)400°C, and (d)500°C

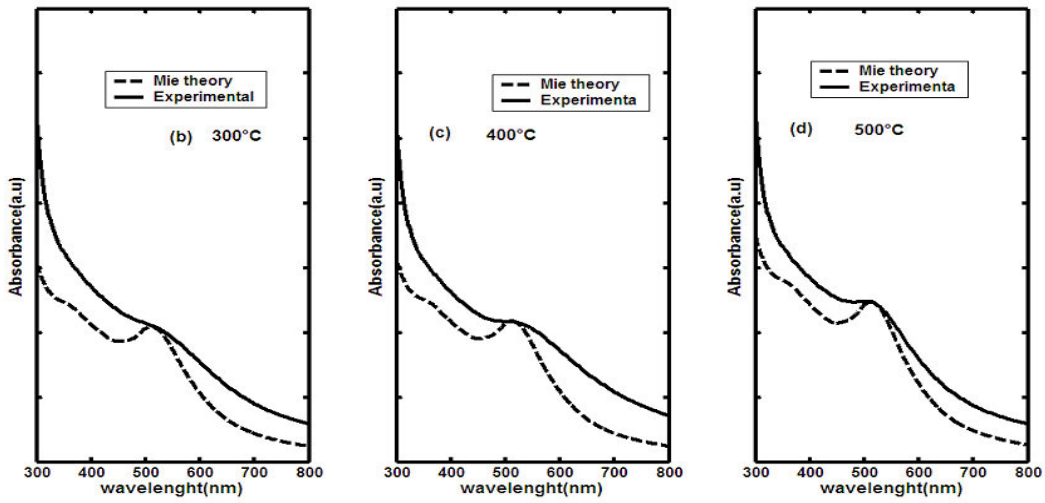


Figure 7: Experimental and Mie simulated optical absorption spectra for the films annealed at (b) 300°C, (c) 400°C and (d) 500°C. Fitting parameters are: curve (b): $D = 2.1$ nm; curve (c): $D = 2.2$ nm; curve (d): $D = 2.3$ nm.

Table1: Fitting results of the XRD spectra of the as-deposited Au/SiO₂ thin films.

2theta (deg)	hkl	FWHM (radians)	Particle size(nm)	d-spacing (nm)	Lattice parameter (Å°)
38.61	(111)	0.169	0.9	2.330	4.035
45.06	(200)	0.250	0.6	2.010	4.020
64.58	(220)	0.205	0.8	1.441	4.075

Table2: Average Au size and lattice constant parameter values calculated from Au (111)

reflections of the annealed samples			
Temperature (°C)	2theta (deg)	Particle size(nm)	Lattice parameter (Å°)
25	38.61	0.9	4.035
300	38.40	1.0	4.056
400	38.29	1.2	4.068
500	38.15	1.5	4.082

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