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Observation of Optical Properties of Gold Thin Films Using Spectroscopic Ellipsometry

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Abstract

In this research work, an attempt has been made to synthesize nano-structured gold thin films over Silicon dioxide (SiO_2) coated on Silicon(Si) Substrate using three deposition techniques namely DC Sputtering, Pulsed DC Sputtering, and Pulsed Laser Deposition(PLD). Optical measurements using spectroscopic ellipsometry showed that the dielectric constants of the films differed between films synthesized by different synthesis routes. This was expected because different synthesis routes yielded different microstructure. The difference in microstructures results in differences in electronic structure and therefore resulting in the differences on the optical response.

Keywords: Gold thin films; GIXRD; Spectroscopic ellipsometry; Pseudo dielectric functions

Introduction

Thin film science [1] and particularly nano-structured has received tremendous attention in recent years. They are being used in various fields of microelectronics, transistors, solar cells, radiation sources, magnetic memory devices, detectors, anti-reflection coating etc. The development of nano-technology [2] and nano-science has made inroads into new trends functional materials. As the size shrinks, the physical properties of the materials also change because of special importance is metallic thin films employed over a range of application areas, including macro electronics and microelectronics. The optical properties of the metallic films [3,4] depend mainly on the free and bound electrons. Most of the metals are transparent in UV and in far UV range except the case of the noble metals where they become transparent in the visible range itself. The difference between noble metals and other metals stems from the fact that the bound electron contribution plays a crucial role in the optical response [5]. Among the metallic thin films, gold has been of considerable interest for years owing to its better performance relative to other metal films [1] for optical applications. The main reason for the application of gold is that it is inertness to oxidation environment. Apart from this, it has some unique mechanical properties like strength, malleability and ductility, good electrical and thermal conductor. It is also known for its ability to endure extreme temperature changes. Nano particle films exhibiting strong Plasmon polarization [2,6] resonance are utilized as optical filters in the sensor applications. Moreover, the ultra thin films can be used in nano-scale electronics and as surface enhanced Raman spectroscopy. While there are several techniques to measure the linear optical properties of gold, spectroscopic ellipsometry [7,8] finds a special place owing to its potential advantages for study of thin films. The technique rests on the fact that, any linearly polarized light upon reflection form a sample becomes elliptically polarized [8,9]. Thus the change in polarization state of the incident light after reflection from the material of interest, their dielectric functions can be determined. It is mainly used in research fabrication to determine properties of layer stacks of thin films and interfaces between the layers. Metallic films in various architectural firms such as thin film, multi-layer, nano-composites, quantum wires, dots etc., find applications in diverse fields ranging from clinical to metallurgical applications [2]. Such a wide range of applications is possible owing to its amenability of being fabricated in such forms. Moreover, the physical properties of thin films are highly dependent on the thickness and dimensions of these films. The properties of materials evolve as one move on from confined structures to bulk forms. Thin films of gold have been deposited by transitional methods such as physical vapour deposition [1]. Recently, varieties of techniques such as electron beam MBE, cluster machines have been employed to deposit films so as to tailor certain specific properties. While sufficient literature is available on the structure and micro-structural aspects of deposited films, there is little literature on the correlation between microstructure and optical properties [5]. Noble metals such as Au, Ag and Cu have been investigated by many researchers owing to the fact that these metals are noble metals and show plasma resonance [2] in the UV-Visible region of the electromagnetic spectrum. Apart from this, these metals have been exploited for applications based on plasmonic resonances. The optical response in metals is explained by the free electron theory. Over and above the free electron behavior, the transition of d electrons to Fermi-level is known to play a vital role in influencing the dielectric response. Therefore, active research is underway to exploit and tune the optical response to various applications. In this direction, several publications are available in literature. According to Svetovoy et al., [10], the optical properties of the metallic thin films have not been measured accurately as it is commonly accepted. Invariably, these properties are taken from handbooks of tabulated data together with the Drude parameters which are necessary to extrapolate the data to low frequencies. The possible reasons may be based upon the fact that the optical properties of the deposited thin films [2,5] depend on the method of preparation, and can differ substantially from the bulk. Careful analysis of the data was performed using ellipsometry [7,8] to extract the values of the Drude parameters. It included joint fits of the real and imaginary parts of the dielectric function, or refractive index and extinction coefficient in the low frequency range, the Kramers-Kronig consistency of the dielectric function or complex refractive index performed at all

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frequencies. The most important conclusions that followed from this analysis were that the dielectric response varied considerably with thicknesses of films. Recently, the interest in the preparation, characterization, and exploitation of the surface-Plasmon resonance (SPR) of the metal nanoparticles, and specifically of gold has grown exponentially to Losurdo et al., [11]. This interest has been driven both by technological applications spanning from biomedicine, sensing and bio sensing to catalysis and to nanophotonics and by the basic physics involved in the size-dependent structural, optical and electronic properties, which can be tailored to be suitable for device applications by the artificially designed geometries that enable the needed functionality for the nanostructures. Therefore, optical properties of gold nanoparticles are still widely investigated. Typically, optical investigations focus mainly on the SPR of Au nanoparticles, and its dependence on the extrinsic effects such as nanoparticles size and shape factor, and the internanoparticles coupling interactions. Indeed, the dielectric function, ε(ω), of metals, and of Au as well, is characterized by the Drude free-electron component, $\varepsilon_{Drude}(\omega)$, and by the interband transitions component, $\varepsilon_{inter}(\omega)$, involving transitions from d levels to an empty state above the Fermi level. i.e., $\varepsilon(\omega) = \varepsilon_{Drude}(\omega)+\varepsilon_{inter}(\omega)$. Although the impact of lattice defects within the nanoparticles as well as non- homogeneous distribution of size and shape of nanoparticles have to be also considered , the predominant size effects on the SPR mainly due to the Drude free electrons, $\varepsilon_{inter}(\omega)$, are extensively investigated. Indeed, the bound electron contribution to the dielectric function also plays an important role in determining Plasmon resonance wavelength and broadening. Nevertheless, there are two aspects that are still critical and interesting from both fundamental and technological points of views worthy of being duly investigated, which are the intrinsic size dependence of the dielectric function of the metal nanoparticles itself and the interconnection of the SPR to the Au nanoparticles interband transition contribution $\varepsilon_{inter}(\omega)$. In recent times research in nanoporous systems are increasing owing to the fact that they exhibit large free surface areas per unit volume compared to the bulk. This property concurs to make porous materials extremely appealing as high-efficiency catalysts and molecular sensors, and has accordingly fuelled huge research efforts in this direction in the past years. Among nanoporous materials, metals are receiving particular attention due to the possibility of exploiting the influence of infinite-size effects on their optical response (Plasmon resonances) for ultrasensitive optical detection. According to Bislo et al., [12] there are remarkable differences between the optical properties of porous materials and their bulk counterparts. After a detailed scan of the literature, we undertook preliminary work on understanding the role of deposition technique in influencing the optical properties of gold thin films.

Experimental

In our experiment, the substrate was taken in such a way that, the type of measurement and study could be intended to be carried out. In our case, for optical study using ellipsometry [7,8] in reflection mode SiO_2 coated on Si was chosen. The substrate was taken from the wafer of P type with <100> orientation with 525 +/- 25 μm thickness and 100 +/- 0.5 mm. diameter. Using diamond cutter the substrate was taken 20 mm × 20 mm. As good adhesion of the films to the substrate is extremely important, therefore we adopted standard procedures for cleaning up of the substrates. In this work, the standard RCA (Radio Corporation of America) procedure was followed, which involved cleaning of substrates with both acidic and basic baths to remove the basic and acidic impurities, respectively. The cleaned substrates were finally stored under isopropyl alcohol in closed container. The thin films of gold of nominal thickness of ≈ 200 nm were then deposited over 200nm SiO2 coated on c-Si by DC Sputtering, Pulsed DC Sputtering, and Pulsed Laser Deposition (PLD), respectively. The measurement of ellipsometric parameters of the films were done by SOPRA ESVG rotating polarizer type spectroscopic ellipsometer in the energy range1.4–5.5 eV in intervals of 10 meV at an angle of incidence of 75°. In ellipsometry, the changes in the amplitude and the phase difference between the parallel(r_p) and perpendicular (r_s) components of the reflected light polarized with respect to the plane of incidence are measured. The change in polarization state of the incident light upon reflection from a sample is measured in terms of the ratios of their amplitudes and phase differences. The ratio, ρ is given by $\rho=r_p/r_s=\tan\Psi .\exp(i\Delta)$ where Ψ is the ratio of the reflection coefficients of the parallel and perpendicular components, while Δ is their phase difference. From the ellipsometric parameters, the optical pseudo-dielectricfunction ε (E) is deduced using the following relation [13].

$$\varepsilon(E) = N_o^2[\sin^2\theta + \left[\frac{1-\rho}{1+\rho}\right]^2 \sin^2\theta \tan^2\theta] \quad (1)$$

Where θ is the angle of incidence, N_o is the refractive index of the ambient and ρ is the ratios of ellipsometric parameters.

Results and Discussion

Figure 1 shows the XRD patterns of Au thin films synthesized by PLD (5000 shots & 30000 shots) and DC Sputtering (deposited for 6 min) technique. The patterns were obtained from STOE diffractometer θ/θ mode at an angle of incidence of 0.5 degree in glancing incidence mode. Sharp diffraction peaks are observed in 2θ angles corresponding to the planes along (111), (200), (220) and (311) planes corresponding to glancing incidence of 0.5. The peaks are such that h+k, h+l and k+l are even and therefore characteristic of face centred cubic (*fcc*) structure. The experimental XRD pattern of Figure 1 matches nearly with JCPDS 04-0784. The JCPDS data show a 100% peak for grain oriented along 111 direction and 52% for (200) planes. However, our experimental data show that the almost equal population of grains oriented along (111) and (220) planes. Similarly there are small differences between the peak positions of the experimental data and the JCPDS data. The different in orientation and the shift in the peak positions are possible owing to the fact that thin films have different growth directions depending on the synthesis conditions. The diffraction peaks were fitted with gaussian profiles and the parameters are tabulated in Table 1.

The grain sizes are calculated by using the Debye-Scherer formula as $D=k\lambda/\beta\cos\theta$, where 'λ 'is the wavelength of X-ray (0.15405 nm), with Cu K_α radiation, 'W' is FWHM (full width at half maximum) in radian, 'θ' is the Bragg's angle, 'D' is the grain size (nm) and 'k' is taken to be 0.9

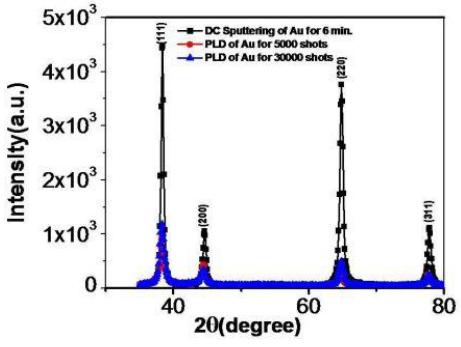

Figure 1: XRD pattern of Au on SiO_2/c-Si for DC Sputtering & PLD.

taken into consideration of spherical particles. In general, broadening of diffraction peaks different factors such as instrument, strain effects, and grain size [14]. Therefore, for an accurate determination of the grain size, one needs to take into account the above factors. The instrumental broadening was determined by obtaining the XRD pattern of standard Si powder whose parameters are very accurately known. The broadening sue to instrument was found to be 0.28126 (0.00381 radian). The XRD patterns were fitted with a gaussian profile in order to obtain the theta and FWHM values. Tables 2-4 show the grain size determination of DC Sputtering of Au on SiO_2 for 6 min and PLD of Au on SiO_2 for 5000 shots and 30000 shots, respectively.

DC sputtering of Au on SiO_2 for 6 min

Table 2 shows determination of grain size for DC Sputtering of Au on SiO_2 for 6 min.

PLD of Au on SiO_2 for 5000 shots

Table 3 represents determination of grain size for PLD of Au on SiO_2 for 5000 shots.

PLD of Au on SiO_2 for 30000 shots

Table 4 represents determination of grain size for PLD of Au on SiO_2 for 30000 shots.

There seems to be wide variation in the grain sizes for different orientation. One possible reason for this could be due to the fact that the strain component has not been considered in fitting the XRD pattern. Thin films indeed how considerable strain depending on the synthesis route.

Figures 2-4 show the ellipsometry parameters tanψ and cosΔ of DC sputterd nanostrucured gold thin films. The tanψ spectrum for 1 and 2 min are very sharp and show maxima and minima. Concomitant peaks are found in the cosΔ values too. The value of cosΔ at +1 or -1 at some definite energies (1.4 eV, 2.75 eV, 3.97 eV, 4.89 eV) indicate the presence of interference. This implies that the films are very thin and the electromagnetic rays as shown in Figure 4 the underlying SiO_2 thereby causing interference. As the film thickness increases, we the decrease in the magnitude of these sharp peaks and therefore moving over to bulk like behavior. A detailed modeling of the optical data was undertaken for select specimens using the nonlinear least

Specimen	(111)	(200)	(220)	(311)
JCPDF	100%	52%	32%	36%
DC sputtering for 6 min	100%	23%	84%	24%
PLD for 5k shots	100%	48%	36.5%	27%
PLD for 30k shots	100%	28.63%	41.37%	19.45%

Table 1: Comparison between JCPDF and experimental data in terms of normalised counts per second.

Sl. No	2 Θ	Θ	cos Θ	FWHM(rad.)	D(nm)
1	38.400	19.2	0.944	0.00292	50
2	44.600	22.3	0.925	0.004691	31
3	64.800	32.4	0.844	0.004375	37
4	77.800	38.9	0.778	0.00521	34

Table 2: Determination of grain size for DC Sputtering of Au on SiO_2 for 6 min.

Sl. No	2Θ	Θ	Cos Θ	FWHM(rad.)	D(nm)
1	38.2	19.1	0.944	0.00646	22
2	44.4	22.2	0.925	0.00308	48
3	64.6	32.3	0.845	0.00426	38
4	77.6	38.8	0.779	0.00618	28

Table 3: Determination of grain size for PLD of Au on SiO_2 for 5000 shots.

Sl. no	2Θ	Θ	Cos Θ	FWHM(rad.)	D(nm)
1	38.3	19.15	0.942	0.00772	19
2	44.3	22.15	0.926	0.01019	14
3	64.8	32.4	0.844	0.00819	20
4	77.5	38.75	0.779	0.00939	18

Table 4: Determination of grain size for PLD of Au on SiO_2 for 30000 shots.

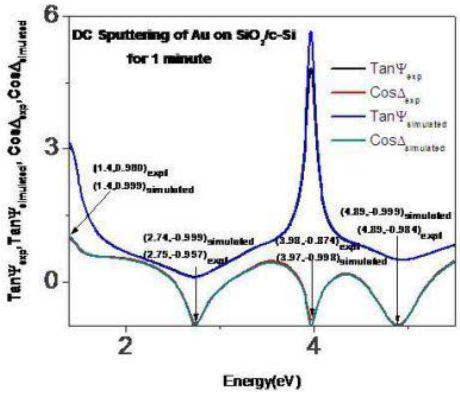

Figure 2: Ellipsometry parameters Tanψ and cosΔ of DC Sputtering of Au on SiO_2 for 1 min at room temperature.

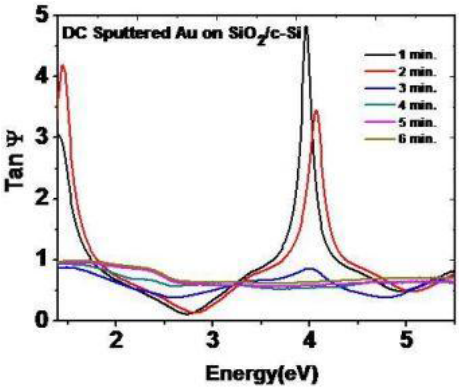

Figure 3: Ellipsometry parameter Tanψ of DC Sputtering of Au on SiO_2 for different deposition time.

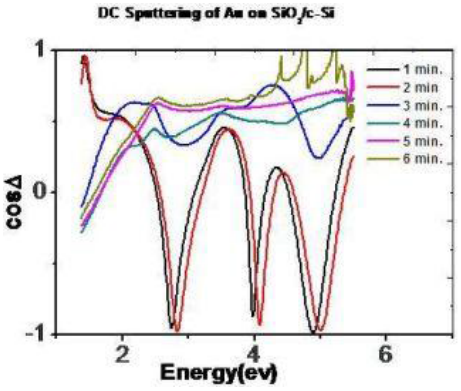

Figure 4: Ellipsometry parameter cosΔ of DC Sputtering of Au on SiO_2 for different deposition time.

square fit method. A four layer model (Figure 5) was incorporated into the model. The refractive index of nano-structured gold was inferred based on a Drude Lorentz model. Two oscillators were used for this purpose. The Drude model was used to fit the data in the low energy region (i.e., below 2.2 eV) while the Lorentz model was used to account for transition of electrons from d-level to the Fermi level. The reference refractive index for gold and SiO_2 was taken from literature. Figure 4 shows the Ellipsometry parameter cosΔ of DC Sputtering of Au on SiO_2 for different deposition time and Figures 6 and 7 show the ellipsometric parameters of gold thin films synthesized by PLD technique. The sharp structures near 4 eV and the zero value near 2.5 eV are clearly an indication of interference. The films are very thin and therefore the electromagnetic waves penetrate the gold and as shown in Figures 6 and 7 the underlying SiO_2 film. As the number of shots increase, we see that the effect due to interference comes down and there is a progressive move towards 'bulk like' feature. Figure 5 shows a representative fit using a four layer model (c-Si/200nm SiO_2/Au film/ambient). The model adopted was a Drude Lorentz combination

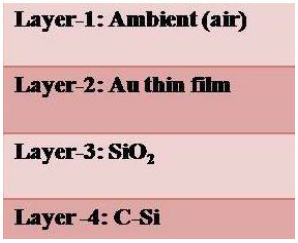

Figure 5: Four layer model.

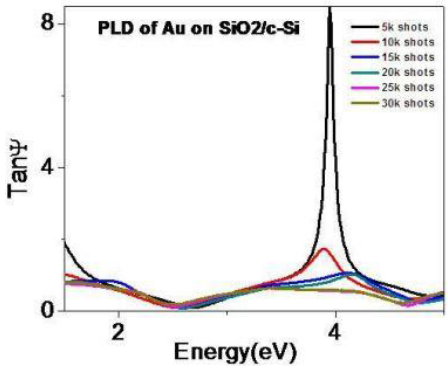

Figure 6: Ellipsometry parameter Tanψ of PLD of Au on SiO_2 for different shots.

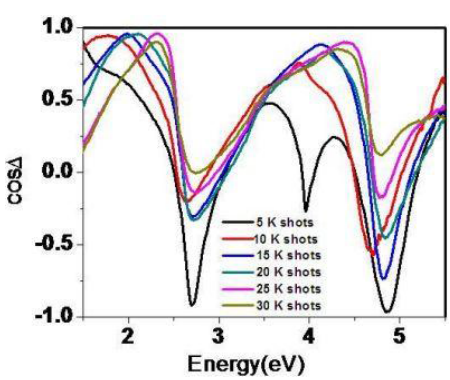

Figure 7: Ellipsometry parameter cosΔ of PLD of Au on SiO_2 for different shots.

wherein the Drude model best fits for the free electron like behaviour and the Lorentz model takes care of electron transition from the d-level to Fermi level. Figure 8 shows the Ellipsometry parameters Tanψ and cosΔ of Pulsed DC Sputtering of Au on SiO_2 for 1 min. It is clear from the figure that, there is no interference effect which signifies the film is thick.

Figures 9 and 10 show the variation of pseudo dielectric function at room temperature for DC Sputtering for 5 min, Pulsed DC Sputtering for 1 min, PLD for 30K shots. The variation of ε_r and ε_i in these films are typical as in the case of nano-structured thin film. Interference effects are seen in the case of PLD deposited samples. The films are not thin

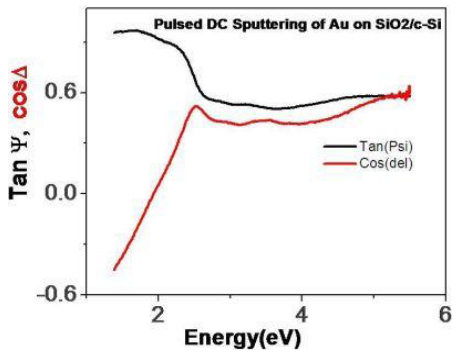

Figure 8: Ellipsometry parameters Tanψ and cosΔ of Pulsed DC Sputtering of Au on SiO_2 for 1 min.

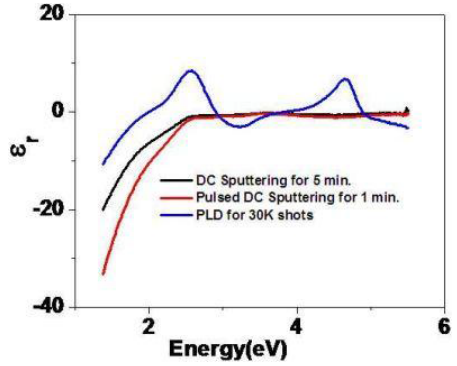

Figure 9: Real part of the experimental pseudo dielectric function of the specimens at room temperature.

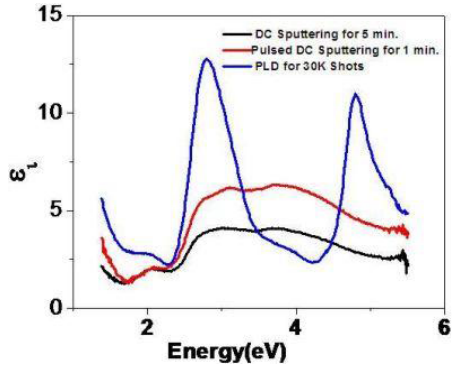

Figure 10: Imaginary part of the experimental pseudo dielectric function of the specimens at room temperature.

so that the SiO_2 is 'seen' by electromagnetic waves, but is thick so as to produce a discernible feature mimicking he bulk dielectric constants. As it is seen the thicker the films, the more negative is the ε_r value at low energy and larger is the value of ε_i at lower energy. The increase of ε_r with film thickness is consistent with the increase in reflection with film. The real and imaginary part of dielectric function shows a distinct change near 2.5 eV which happens to be the plasma frequency of the electrons. The typical negative value of the real part below 2.5 eV indicates that the free electrons are responsible for the optical properties. Below 2.5 eV, the specimens are reflecting while above 2.5 eV, there is a significant absorption (as seen in imaginary part). The increased absorption in this region is owing to the transition of electrons from d-level to the Fermi level.

Conclusion

Thin films were synthesized using different deposition techniques like DC sputtering, Pulsed DC Sputtering and Pulse Laser Deposition (PLD). Structural characterization of the films using glancing incidence X-ray diffraction showed that the films were *fcc* nature and compared well with star quality JCPDF data. The grain sizes computed from the Debye-Scherer formula showed that the grain sizes were more uniform for the specimens prepared by PLD technique using 30,000 shots. The difference in orientation and shift in the peaks were found owing to the fact that thin films have been adopted under different synthesis conditions. Optical measurements using spectroscopic ellipsometry showed that the dielectric constants of the films differed between films synthesized by different synthesis routes. This was expected because different synthesis routes yielded different microstructure. The difference in microstructures results in differences in electronic structure and therefore resulting in the differences on the optical response. Future direction in terms of the electrical resistivity measurements as a function of thickness of films can be performed in order to understand the evolution of the films from the nucleation and growth stage towards film formation. This will also throw light on the correlation between microstructure and the transport properties. Optical investigations at high and low temperatures can also be accomplished in order to discern the correlation between microstructure and the dielectric constants and to compute the thermo-optic coefficients. This quantity can be an important parameter for applications involving nanostructures at elevated temperatures.

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