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 (SiO₂) 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 wave lengths.

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mainly due to the Drude free electrons, \( \varepsilon_{\text{inter}}(\omega) \), are extensively have to be also considered, the predominant size effects on the SPR as non-homogeneous distribution of size and shape of nanoparticles thin films.

In our experiment, the substrate was taken in such a way that, the grain sizes are calculated by using the Debye-Scherer formula as

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

where \( \lambda \) is the wavelength of X-ray (0.15405 nm), with Cu K\(_\alpha\) radiation, \( W \) is FWHM (full width at half maximum) in radian, \( \theta \) is the Bragg’s angle, \( D \) is the grain size (nm) and \( K \) is taken to be 0.9

**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 c-Si was chosen. The substrate was taken from the wafer 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 c-Si was chosen. The substrate was taken from the wafer 100 +/- 0.5 mm. diameter. Using diamond cutter the substrate was taken 20 mm \( \times \) 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.
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 due 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 SiO₂ for 6 min and PLD of Au on SiO₂ for 5000 shots and 30000 shots, respectively.

**DC sputtering of Au on SiO₂ for 6 min**

Table 2 shows determination of grain size for DC Sputtering of Au on SiO₂ for 6 min.

**PLD of Au on SiO₂ for 5000 shots**

Table 3 represents determination of grain size for PLD of Au on SiO₂ for 5000 shots.

**PLD of Au on SiO₂ for 30000 shots**

Table 4 represents determination of grain size for PLD of Au on SiO₂ 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 have considerable strain depending on the synthesis route.

Figures 2–4 show the ellipsometry parameters tanψ and cosΔ of DC sputtered nanostructured 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 SiO₂ 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
wherein the Drude model best fits for the free electron like behaviour and the Lorentz model takes care of electron transition from d-level to Fermi level. Figure 8 shows the Ellipsometry parameters $\tan \psi$ and $\cos \Delta$ 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 $\varepsilon_r$ and $\varepsilon_i$ 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 enough for the 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 $\cos \Delta$ 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 model.
so that the SiO₂ is ‘seen’ by electromagnetic waves, but is thick so as to produce a discernible feature mimicking bulk dielectric constants. As it is seen the thicker the films, the more negative is the εᵣ value at low energy and larger is the value of εᵢ at lower energy. The increase of εᵣ 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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**References**