

Modeling & Simulation of Nano film thickness of Gold deposited by Thermal Evaporation Process (TEP)

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Article Info

Article history:

Received 2 March 2014

Received in revised form

10 April 2014

Accepted 30 May 2014

Available online 15 June 2014

Keywords

Physical Vapor Deposition,
Modeling,

Film Thickness Simulation,

Gold Evaporation,

Thin Film Deposition

Abstract

The surface temperature is required to specifying the temperature of the evaporating gold using constant elements for turn off the refinement in the post-processing settings. The paper represents the modeling of nano scale gold film by computing the film thickness, mass deposited on the substrate and mass transfer rate with time dependent model using BDF solver. Gold is evaporated from a resistively heated evaporator source at a temperature of 2000K onto a surface held on a fixed surface. The film thickness varies between 34nm to 39 nm across the sample after 60 sec of deposition, with radial symmetry about the midpoint of the source. The film thickness as well as mass deposited at a point increases linearly with time. Since the angular distribution is of particular interest in this model, by increasing the integration resolution to a maximum value for ensuring the most accurate angular resolution when computing the flux.

1. Introduction

The nanoscale gold film thickness has found newer capabilities in different fields of science and technology such as coating glasses/mica to change their properties and many coloured optical coding for biological assays Gold nanometer thick film is being used to enhance electroluminescence and quantum efficiency in light emitting diodes. Besides signal amplification, nanometer thick gold film evolved new types of new sensors that are capable of detecting very small amounts of analytes such as chemical vapours in the scale of few ppm. Adeleh Granmayeh Rad et al [1] discussed the usage of gold nano film is in making advanced dyes and pigments. Sometimes gold nano film has been used to dye textiles, support to supply clean energy (by solar cell) and high density data storage (flash memories and discs Gold nanoscale film quality of non-toxic and biocompatibility both in vivo and in vitro environments makes useful in biomedical applications. The unique properties of gold nanoscale structured materials supply good opportunity for coordinating biological identification events with electronic signal transduction and for making an evolution of bioelectronics devices with newer features. Gold in nanoscales have been found for potential candidates to support in photo-thermal therapy and radiotherapy. Optical and electronic properties of gold can be utilized to improve the contrast in molecular imaging for the detection of cancer initially. Gold-based technologies also help to facilitate a ultimate needle-free delivery system, a technique that used gold and permitted vaccines to be supplied through the skin producing use of the fact that small particles can go through gaps between cells while large ones cannot. Gold nanoscale-based technologies give solution to some of environmentally great issues, such as ecofriendly production methods, pollution control and water purification. No doubt gold is really one of the non-reactive metals, and it is resistant to oxidation.). Ragini Raj

Singh et al [8] discussed gold is also used in Photovoltaic HgCdTe Mid wavelength Infra-red detector to make ohmic contacts to find out the passivation characteristics of CdS/HgCdTe structure using C-V measurements.

Ali Moarrefzadeh [2] discussed that Physical vapor deposition (PVD) includes a wide range of vacuum coating processes in which material is physically taken out from a source by evaporation or sputtering, transported through a vacuum or partial vacuum by the energy of the vapor particles, and condensed as a film on the surfaces of appropriately placed parts or substrates. A group of very versatile coating processes in which a material is converted to its vapor phases in a vacuum chamber and condensed onto a substrate surface as a very thin film (upto 1µm thickness). The deposition of thin film layers from the vapor phase is done through several methods.

Gold deposition depending upon the different applications as well as the suitability of the process requirement and availability of resources can be done in following ways:

Wenjun Zhou et.al [4] discussed the Chemical vapour deposition (CVD) generally uses a gas-phase precursor, often a halide or hydride of the element to be deposited. In the case of MOCVD, an organometallic gas is used. Commercial techniques often use very low pressures of precursor gas. The chamber is first evacuated to a vacuum of around 5m torr and substrate temperature fixed to 350°C. Now evaporator is resistively heated to a temperature of about 160°C to start volatilization of the precursor. The deposited precursor then thermally decomposes into pure gold by a reaction above 300°C. The thickness of the gold film can be controlled by adjusting the amount of precursor, the temperature of the deposition chamber, and the location of the samples to be coated relative to the inlet of the evaporator into the deposition chamber. Generally gold precursor is thermally stable between 150 and 300 °C. Keewah Chan [5] discussed that gold can be deposited on silicon or quartz by rf sputtering by using DC sputter coating system. The rf power can of several hundred watt, substrate temperature about 300 °C

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with a vacuum of 1mbar order or better for time depending upon the thickness required, say for nanometer thickness 1 hour.

Carl E. Larson [6] discussed that gold deposition of high purity gold onto various substrates from dimethyl-2fl-pentandionato gold (III), $\text{Me}_2\text{Au}(\text{acac})$, by localized, laser-induced (photothermal) chemical vapor deposition. CVD of gold from dimethyl-(1,1,1-trifluoro-2,4-pentandionato) gold (III) and dimethyl-(1,1,1,5,5,5-hexafluoro-2,4-pentandionato) gold (III), $\text{Me}_2\text{Au}(\text{tfac})$ and $\text{Me}_2\text{Au}(\text{hfac})$ complex can be done in a stainless steel vacuum chamber evacuated by a turbomolecular/diffusion/cryo pump to a base pressure of $< 10^{-6}$ torr. A flow of argon or nitrogen carrier gas through a Pyrex vessel containing the gold complex at room temperature is used to deliver the organogold precursor into the chamber through stainless steel lines. Chamber vacuum and carrier gas flow rate could be varied independently. Deposition proceeds on a substrate placed in the chamber in the flow path of the carrier gas and heated by a copper block heater with temperature controller. Miroslav Gojo et al [7] discussed that gold can be deposited in a thermostatically controlled electrode cells in a electrodeposition Cell has two openings, one for thermometer another for nitrogen inlet for purging the oxygen out of the electrolyte keeping pH value 5 to 7 and each silicon wafer piece coated and alloyed with gold as working electrode, filled with chosen electrolyte warmed upto a given temperature and purged with nitrogen. Gold deposited by electrochemical method has higher purity, lower permeability and good adhesion to the substrate. Anne-Felicie Lamic-Humblot et al[10] discussed that gold can be very easily deposited at ambient pressure and in distilled water with magnetic rod stirring, followed by thermal treatment from Tetrachloroauric acid and urea. This paper mainly deals with simulation & modeling of time dependent PVD model.

Though a lot of research work has been done on the evolution of gold film deposited on nanoscale or higher thickness by different deposition process through different sources (resistively, sputtering, E-beam, magnetron, radio frequency) in different baskets/crucibles at different temperatures and modeled mostly with direct simulation Monte Carlo. Also these methods solve in the volumes of the modeled and geometries. Number densities found to be not accurate and precise. Ineligible simulation for the accurate modeling of low pressure, low velocity gas flows in complex geometries. These studies subjected to statistical scatter. Moreover, these could not completely explained free molecular flow interface and applied dsmc computes the trajectories of large numbers of randomized particles through the system, but introduces statistical noise to the modeling process and also the method is slower. The objectives of paper is to explain the free molecular flow interface in low pressure low velocity gas flow using simulation and time dependent modeling to influence of evaporation process parameters.

2. Experimental Study of Thermal Evaporation Process

We study and analyze the physical vapor deposition techniques and equipments that are in common use in the large scale production of coatings that find uses in the

optical, display, decorative, tribological, and energy-generating /saving industries. Evaporating materials are classified as dielectric compounds, metals, alloys, or mixtures. The same evaporant material can exhibit different optical, electrical, and mechanical properties depending on the deposition process. Titanium oxide is a unique example of a metal oxide compound that, depending on deposition process parameters, can be made into film layers that are: transparent, electrically conductive, chemically reactive to light and bio- agents, chemically inert, or exhibit spectrally selective absorption. The dependent parameters are starting composition, oxidation state, and crystalline structure and packing density.

PVD techniques used generally are basically two in nature: thermal evaporation by resistively heating or by using an electron- beam heating, and sputtering, a non thermal process. Alterations and accompaniments are made to the basic thermal evaporation technique to permit different coating materials and substrate types to be included.

Process additions designed to alter the growth nano-structure or composition of the film through control of the dependent variables listed above include bombardment of the growing film by high energy inert- or / and reactive ions, substrate heating, atmosphere composition and partial pressure, rate, and vapor incidence angle. A further important variable contribution to the nucleation and self-assembling growth structure of the condensing ad atoms, that we have discussed frequently, is the condition both chemical and physical of the substrate surface.

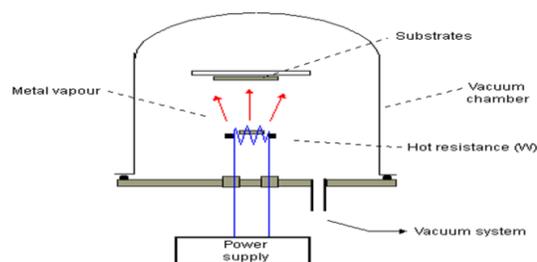


Fig. 1. Vacuum Coating Process Diagram

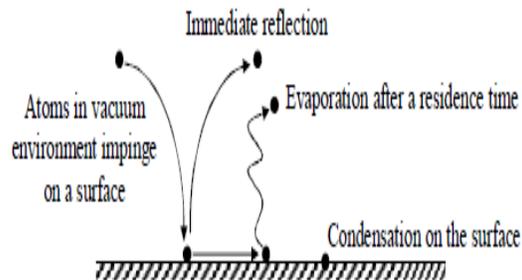


Fig. 2. Thermal Evaporation Process

Varieties of coatings can be deposited such as metals, alloys, ceramics and other inorganic compounds, and even certain polymers. Deposition can be done onto the varieties of substrates such as metals, glass, and plastics. The properties of atavistically deposited films depend strongly on:

- The material being deposited
- Substrate surface chemistry and morphology
- The surface preparation process
- The details of deposition process and the deposition Parameters
- mean free path of evaporant
- source to substrate distance
- vapor pressure
- sticking coefficient

Condensation and nucleation- Atoms that impinge on a surface in a vacuum environment may be reflected immediately, re-evaporate after a residence time, or condense on the surface shown in figure 2. Mean free path is the minimum distance between two successive collisions and is given by formula depending upon the vacuum in the chamber:

$$\lambda = \frac{k_B T_c}{\sqrt{2\pi} \cdot P \cdot d^2}$$

Where T – usually room temperature of chamber

P – Vacuum in chamber

At 300 K

d - diameter of vapor atom ~2-5 Å

$$\lambda = \frac{5 \times 10^{-3}}{P_T (\text{Torr})} \text{ cm}$$

Based on this mean free path source to substrate distance is optimized for constant flux and better deposited film quality. Vapor pressure varies depending upon the source temperature and is different for different materials, for suitability standard plot [11] is provided from which depending upon source material vapor pressure is selected. Sticking coefficient is defined as the ratio of the condensing atoms to impinging atoms. If the atoms do not immediately react with the surface, they will have some degree of surface mobility over the surface before they condense.

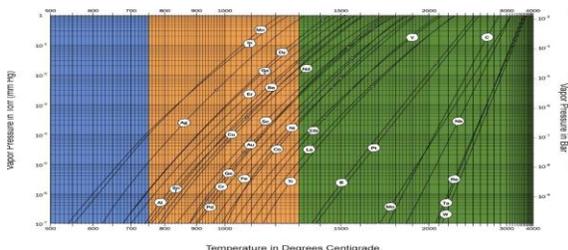


Fig: 3. Graph between Vapor Pressure of Source Vs Temperature

Re-evaporation is a function of bonding energy between the adatom and the surface, the surface temperature, and the flux of mobile adatoms. Example: The deposition of cadmium on a steel surface having a temperature greater than about 200 °C will result in total re-evaporation of the cadmium.

2.1 Surface Mobility

The energy of the atom, atom-surface interaction

(chemical bonding) and the temperature of the surface influence the capability of an atom on a surface. The mobility on a surface can change because of variations in chemistry or crystallography. The various crystallographic plates of a surface have different surface free energies that influence the surface diffusion.

Atoms condense on a surface by losing energy. They lose energy by:

- Forming and breaking chemical bonds with the substrate atoms.
- Finding preferential nucleation sites (lattice defects, atoms steps, and impurities)
- Interacting with another diffusing surface atoms (same species)
- Colliding or reacting with adsorbed surface species. Atoms form nuclei after condensation. Homogenous nucleation is said to occur if the surface is of same material as the deposition atoms and if they are different materials, the process is called heterogeneous. In semiconductor field, heterogeneous nucleation forms heterojunctions. G.H. Gilmer et al [3] discussed that three types of nucleation mechanisms have been identified; they differ according to nature of interaction between the posited atoms and the substrate material:

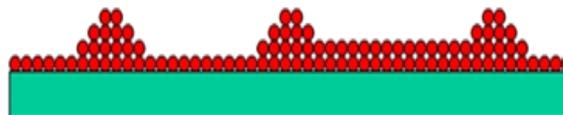
Frank-Van der Merwe mechanism leading to a monolayer- by-monolayer growth (layer growth; ideal epitaxy)



Volmer-Weber (V-W) mechanism, characterized by a three-dimensional nucleation and growth (island growth)



Stranski-Krastanov (S-K) mechanism, where an altered surface layer is formed by reaction with the deposited material to generate a strained or pseudomorphic structure, followed by nucleation on this layer (Layer + island growth)



Nuclei coalescence and agglomeration the nuclei develop by collecting atoms that diffuse over the surface. Isolated nuclei grow laterally and vertically on the surface to form a continuous film and less amount of material is needed if nucleation density is high. The major growth mode of nuclei may be: -laterally over the substrate surface (wetting growth) such as gold on copper and chromium, iron on W-O surfaces, and titanium on SiO2 the nuclei may prefer to grow in a vertical mode (dewetting growth) such as nickel and copper on W-O surfaces, and gold on carbon, Al2O3, and SiO2. M.Levin et al [9] discussed that the substrate temperature also critical in thin film deposition.

2.2 PVD Film Evaluation

Deposited films are typically evaluated for visual defects, thickness, and adhesion. Visual defects such as bare spots, small voids, incorporated flakes, or debris can be observed with a stereo microscope having a magnification of 10 to 100 times. Film thickness is generally measured by one of the following methods: Thickness of film as modeled can be simulated experimentally with dektek surface profilometer based on LVDT principle with diamond size of 12.5 μ m radius stylus. Polished metallurgical micro sections are used to microscopically observe the coating thickness on various part surfaces. This method is the most direct way to determine thickness uniformity. Beta (high-energy electron) backscatter instruments are used to measure the film thickness nondestructively. This is an indirect method that requires calibration with a known standard; substantial errors can be made in measuring the film thickness on curved surfaces if care is not exercised. A ball-crater instrument can be used to polish through the surface of a coating. The relationships between the diameters of the polishing ball, the maximum diameter that shows the effects of polishing, and the diameter of the substrate area that is exposed by polishing is used to calculate the thickness. Coatings that are up to 120 m-in. (3Mm) thick can be measured with an accuracy of ± 4 m-in. (± 0.1 Mm) without difficulty on relatively smooth, flat or cylindrical surfaces. The adhesion between coating and substrate is difficult to measure directly for highly adherent films; pull tape tests capable of measuring yield strengths that are typical of metals and PVD hard coatings on metals have not been developed. In stone abrasion test, a fine sharpening stone is rubbed back and forth across the coated surface, allowing the stone particles to make grooves in the surface by nonrealistic deformation. The film is then inspected under a microscope to obtain adhesion information.

3. Experimental Observations

The island gold films were prepared using a laboratory thermal evaporation setup working at residual vacuum of (2.5 - 4) $\times 10^{-6}$ mbar. The deposition setup was equipped with the two-stage vacuum system based on the diffusion pump (oil based), turbomolecular or cryopump alongwith rotary vane pump or rotary screw pump (oil free). In case of oil based pumps the ultimate vacuum achieved in the system depends upon the vapor pressure of the oil used in pumps, generally Silicone based oils are used to achieve vacuum of 1.0×10^{-6} order in the chamber. Sometimes high discharge Ar gas plasma substrate cleaning can be done at vacuum of 5×10^{-3} mbar, if needed. M.Levlin et al [9] discussed that annealing before evaporation affects the surface of substrate and removed the adsorbed molecules. The films were deposited on the substrates cleaned in the ultrasound bath in isopropyl alcohol and drained by a compressed air flux. During the deposition, all substrates were kept at room temperature i.e no substrate heating or cooling. Gold films were evaporated at residual vacuum from tungsten baskets at temperature of 2000° K. Deposition was provided up to full evaporation of material from the tungsten boat. Portions of the material for evaporation were prepared with help of the microbalance ViBRA. Value of this mass was found by calculation from

the defined (nominal) film thickness using following relation for the point evaporation source:

$$t = M \cos \theta / 4 \pi \rho r^2$$

Here t is the nominal film thickness, M is the mass of the evaporated material, ρ is the material density, r is the distance between an evaporation source and a substrate, and θ is the deposition angle defined by geometry of the substrate. It should be noted, that this formula can be used only for rough estimation of an average thickness of ultra-thin films. In this case, certain assumptions about the structure of the film, the shape and size of the islands, can be made only on the basis of measurement of electrical and optical properties of this film and topographic surveillance using SEM or AFM. Optical absorption and transmittance of gold films on glass substrates were measured in wavelength range from 200 to 1100 nm using the 640 FT IR spectrometer. F.Sharipov et al [12, 13] discussed that flow regimes are categorized quantitatively via the Knudsen number (Kn), which represents the ratio of the molecular mean free path to the flow geometry size for gases:

Table: 1. Classification of Flow Regimes

Flow type	Knudsen Number
Continuum flow	Kn < 0.01
Slip flow	0.01 < Kn < 0.1
Transitional flow	0.1 < Kn < 10
Free molecular flow	Kn > 10

4. Model Description

General description of the model is presented in fig. 1 where low pressure gas flow in vacuum system i.e molecular flow and it can be seen that the model inputs are ambient temperature, evaporant(gold) temperature, vapour pressure, molecular weight, density of gold, neglecting the substrate surface temperature. The Free Molecular Flow interface uses the angular coefficient method to model flows with Knudsen numbers Kn > 10. This physics interface avoids solving the physics in the volumes of the modeled geometries, and requires meshing only of the surfaces. Completely diffuse scattering (total accommodation) and emission are assumed at all surfaces in the geometry, and flow is computed by integrating the flux arriving at a surface from all other surfaces in its line-of-sight. This means that the dependent variables exist only on the surfaces of the geometry, and the solution process is much faster than the dsmc method. In this model the number density and pressure of the deposited species are of limited interest and will not be computed. Furthermore, it is not subject to statistical scatter. Number densities are reconstructed using a method included in the Free Molecular Flow interface. The Molecular Flow Module is designed to offer previously unavailable simulation capabilities for the accurate modeling of low pressure, low velocity gas flows in complex geometries. It is ideal for the simulation of vacuum systems including those used in semiconductor processing, particle accelerators and mass spectrometers. Small channel applications (e.g. shale gas exploration and flow in nanoporous materials) can also be addressed. The Molecular Flow Module uses a fast angular coefficient method to simulate steady-state free molecular

flows. We can model isothermal and non-isothermal molecular flows, and automatically calculate the heat flux contribution from the gas molecules. The discrete velocity method is also included in the module for the simulation of transitional flows. Historically, flows in this regime have been modeled by the direct simulation Monte Carlo method. This computes the trajectories of large numbers of randomized particles through the system, but introduces statistical noise to the modeling process. For low velocity flows, such as those encountered in vacuum systems, the noise introduced by dsmc renders the simulations unfeasible. COMSOL uses alternative approaches: employing a discrete velocity method for transitional flows (using a Lattice Boltzmann velocity quadrature) and the angular coefficient method for molecular flows. Using the input parameters, the model computes the thickness of gold deposited, mass deposited on the surface of substrate, and mass transfer rate by using COMSOL software. The following wall conditions in terms of wall, outgassing wall, adsorption/desorption, deposition are inbuilt in COMSOL software: In adsorption/desorption boundary condition, sticking coefficient can be defined along with other condition. Gold is placed in resistively heated Tungsten boat which is having very high melting point of 3420^0 C. Substrate is one quarter of a 4" wafer mounted on stationary support on top of tungsten boat depending upon the mean free path and Langmuire-Kundsen relation. A screen is placed to cover the substrate, if more than one source is used.

Table 2. Input Parameter for the Model

Name	Expression	Value	Description
Tamb	293.15[K]	293.2 K	Ambient temperature
Tevap	2000[K]	2000 K	Evaporation temperature
pvap	50[Pa]	50.00 Pa	Vapor pressure of gold
Mn0	197[g/mol]	0.1970 kg/mol	Molecular weight of gold
Rho0	19.3 gc/m ³	1.930E4 kg/m ³	Density of Gold

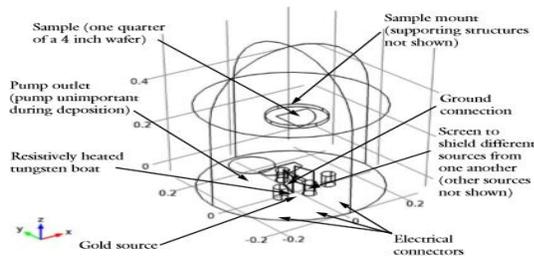


Fig. 4. Model Geometry Various Components of Evaporator

5. Result & Discussion

In table 2 various input parameter required for the model are given to compute the molecular flow in vacuum system. Generally, the ambient temperature is fixed based on the experimental setup or experimental conditions but the evaporation temperature can be varied as per the thickness or mass transfer to be deposited on the substrate. This evaporation temperature can be increased or decreased depending considering the vapor pressure, to make fast the mass transfer keeping the good adhesion with uniformity on the substrate surface.

Figure 5 shows the flux of gold molecules on the surfaces of the model. This constant flux determines the thickness of gold deposited shown in figure 6. In figure 6, it is obvious the film thickness is maximum in the centre of substrate positioned directly on vertically centre of tungsten boat/source, greater than 38.5 nm after 60 seconds of thermal evaporation process. This thickness decreases radially outwards surface of the substrate 34.28 nm.

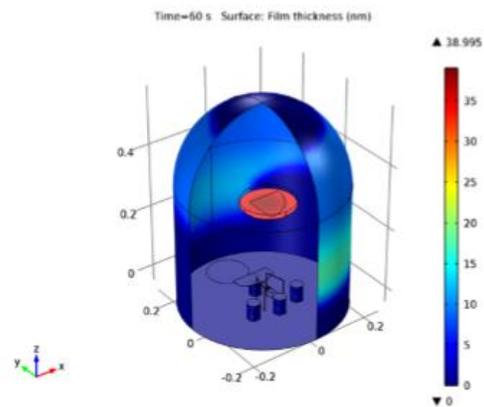


Fig. 5. Film Thickness on the Surfaces, After 60 s of Deposition

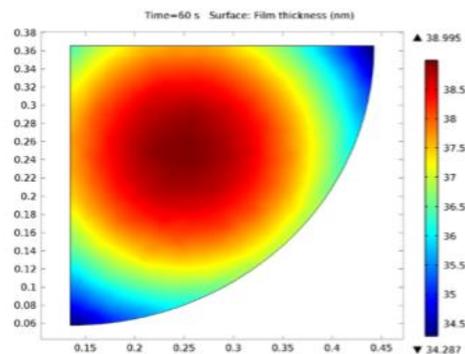


Fig. 6. Film Thickness on the Sample, After 60s of Deposition

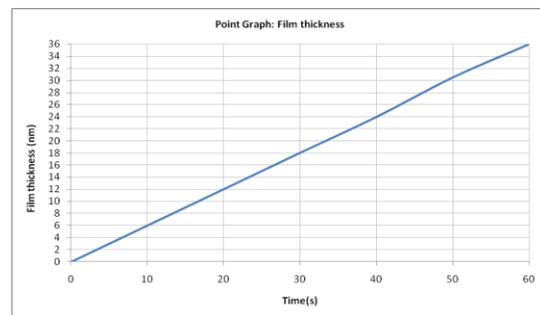


Fig. 7. Time Dependent Variation of Film Thickness

In Figure 7 based the molecular flux deposited on substrate ,graph shows the gold deposited thickness after 60 seconds from initial condition of zero second. It is clear from graph that the film thickness varies linearly with time.

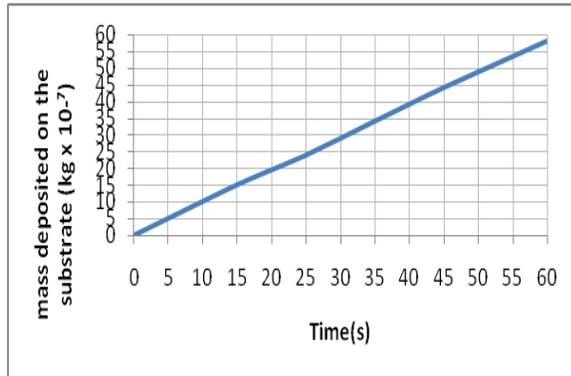


Fig: 8. Time Dependent Variation of Mass Deposited on the Substrate with Time (Sec.)

In figure 8 graph is plotted with time for mass ($\text{kg} \times \text{E}-7$) deposited on the surface of substrate and shows that as mass deposited on substrate increases with time as in the case of figure 7 since the depositing thickness with time adds mass also on the substrate. In figure 9 mass transfer rate ($\text{kg} \times \text{E}-4/\text{sec}$) is plotted for 60 seconds and is a straight constant abscissa parallel line. Only the flux is required to compute the deposition rate, but in this instance, since most of the computational time is used to compute the view factors, solving the time dependent problem adds little additional time to the solution process. Using a time dependent model also allows for more advanced extensions of the model, for example, re-evaporation of gold from hot surface close to the evaporative source could be included.

Certainly, loss of gold is there during thermal evaporation process for 60 seconds. It is based on the simple yield phenomenon of difference between the input gold put on boat, deposited on substrate and residual gold in the tungsten boat. This shows indirectly how much efficient is our process to achieve the desired target with a

References

- [1] Adeleh Granmayeh, et.al., Gold Nanoparticles: Synthesising, Characterizing and Reviewing Novel Application in Recent Years, Physics Procedia 22, 2011, 203 – 208
- [2] Ali Moarrefzadeh, Simulation and Modeling of Physical Vapor Deposition (PVD) Process Wseas Transactions on Applied and Theoretical Mechanics, 7(2), 2012
- [3] G.H. Gilmer et.a., Thin film deposition: fundamentals and modeling ,J of Computational Materials Science 12, 1998, 354-380
- [4] Wenjun Zhou, Effective Permittivity of Ultrathin Chemical Vapor Deposited Gold Films on Optical Fibers at Infrared Wavelengths, J. Phys. Chem. C, 118, 2014, 670–678
- [5] Keewah Chan, et.al., Formation of gold nanoparticles in silicon suboxide films prepared by plasma enhanced chemical vapour deposition J of thin solid films, 519, 2011, 4952-4957
- [6] Carl E. Larson, et.al., Chemical Vapor Deposition of

way to find out further reduce this loss by establishing the controlled process parameters.

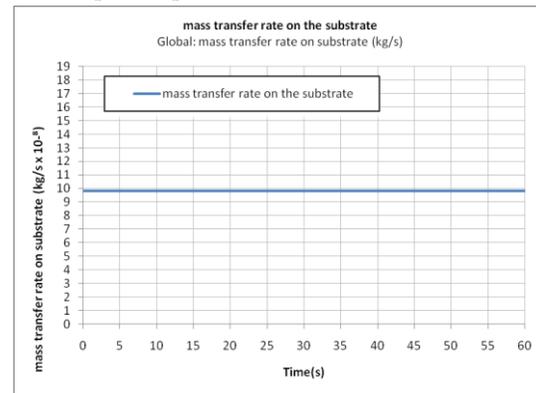


Fig: 9. Variation of Mass Transfer Rate with Time

6. Conclusion

The deposited film thickness on the substrate and the chamber wall is computed. For optimized method as well as for fast and accurate simulations, gases at low pressures cannot be modeled using conventional computational fluid dynamics tools. That is due to the fact that kinetic effects become important as the mean free path of the gas molecules becomes comparable to the length scale of the flow. Coatings of gold having good uniformity & appropriate thickness have been produced on stationary, non-rotated, flat substrates using a vacuum thermal evaporation technique. The thickness uniformity around the substrate was a sensitive function of the mean free path as well as evaporant incidence angle. Also to increase the rate of evaporation we have to raise the temperature of the source.

The following conclusions can be obtained:

- i) The gold film thickness increases with time
- ii) The mass deposited increases with time
- iii) Thickness variation across the substrate surface follows cosine distribution due to incident angle

- Gold, IBM Almaden Research Center, San Jose, California 95120, 1986
- [7] Miroslav Gojo, et.al, Electrochemical Deposition of Gold in Citrate Solution Containing Thallium, Acta Chim. Slov, 55, 2008, 330–337
- [8] Ragini Raj Singh, et.al, Investigation of passivation processes for HgCdTe/CdS structure for infrared application, 510, 2006, 235–240
- [9] M. Levlin, et al, Evaporation of gold thin films on mica: effect of evaporation parameters, 115, 1997, 31–38
- [10] Anne-Felicie Lamic-Humblot, et.al, An easy way to obtain thin film on silica glass substrate by chemical method, 539, 2013, 151–153
- [11] Authur K.Burak Ucer, Vacuum evaporation, www.users.wfu.edu
- [12] F.Sharipov, Universidade Federal do parana, Curitiba, 81531-900, Brazil <http://fisica.ufpr.br/sharipov>
- [13] Yu. A. Anikin et. al(2012) Development of applied software for analysis of gas flows in vacuum devices, 86, 1770-1777