Investigation of Gold Nanostructures on Silicon Using Electrochemical Deposition Method

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Abstract

Nanostructures of gold electrodeposited on silicon (100) substrate with two electrode homemade cell were investigated. In this paper we report our experimental results of gold-electroplating using a sulfite-based electrolyte instead of toxic gold-cyanide. The used electrolyte was safe and friendly environmental. Film thickness as a function of current density and deposition rate were calculated using gravity method. An empirical formula was satisfied the expected deposition thicknesses. Deposition rate of ≈ 5-40nm/ min was achieved. Au (111) structure for gold nanofilm was characterized by XRD. Morphology of gold film deposited was investigated with AFM. Morphology of Au thin films on silicon shows nanosize particles after annealing process at 600°C.

Keywords: Gold electroplating, Gold islands, Gold nanostructure, Au film Annealing.

Introduction

Gold structures on silicon (Si) substrates in the form of thin films nowadays are used in vast range of applications such as microelectromechanical and nanoelectromechanical systems [1,2], sensors [3], electronic textile [4], bioengineering [5], generator of nonlinear optical properties [6], or devices for surface-enhanced Raman scattering [7]. Ultrathin gold film can generally be produced by various methods including thermal evaporation [8], electrochemical deposition [9, 10], and electroless deposition [11]. Nanoparticles have been assembled on silicon by deposition using pulsed laser [12], electrochemistry [13], microwave [14], and thermal heating of evaporated thin film [15]. Gold clusters were prepared by condensing evaporated gold in nanometer –sized performed on the surface of highly oriented pyrolytic graphite (HOPG) [16]. Metal islands and thin films have been formed by sputtering [17], and evaporation onto chemically modified glass substrate [18]. Strongly bond and high stable gold island films on glass are obtained by a simple one step preparation procedure based on high temperature annealing and partial embedding of gold nanostructures evaporated on glass, providing stable and effective localized plasmon transducers [19]. Formation of nanoislands on microscopic glass was monitored with UV-visible spectroscopy, cyclic voltammetry, and atomic force microscopy methods [20]. Gold nanoislands film also prepared on glass by thermal evaporation of organic matters [21]. Thin film (20nm) of gold evaporated on glass then annealed in oxygen produced rounded islands [22].

The aim of this work is to find simple, cheap, safe, friendly environmental and controllable film thickness procedure to produce homogenous ultrathin gold nanofilm on silicon substrate. We believe that electrochemical deposition process could be used for such purpose in addition to the possibility of film thickness determination study by galvanic method.

Experimental:

Substrate cleaning:

Silicon (100) substrates (p-type), size 1.5x1.0X0.5 cm^3 were cleaned for 5 min. with carbon tetrachloride, acetone and alcohol, then treated with H_2SO_4 : H_2O_2 (1:1), and dipped in 10٪ buffer HF solution for 3 min to remove the surface native oxides. After dried in a flux of N_2 gas, 1cm^2 of the sample was immersed into the electrolyte as anode immediately.

Experimental set up:

The used apparatus is a simple electrolytic cell with DC source and has no need for vacuum equipment. Two electrode electrochemical cell with high purity gold strip (dimension- 2x0.5x30mm^3) as an anode and 1x2 cm^2 silicon substrate (100) as a cathode were used. The gold electrolyte solution of 100ml was prepared from 0.5M H_2SO_4 and 0.5mM of NaAuCl4. D.C power supply (Model: PS – 305D / China, 0-15volt) with fine and accurate voltage adjustment was used. Solution temperature was controlled measured by mercury thermometer. Digital millimeter (A830L/ USA) was used to measure the current in milli-ampere. Stirrer hot plate (Digital instrument EQ-SP-131320Q/ USA) was used for heating and mixing the solution at medium stirring rate (400 rpm) throughout the experiment.

Electrochemical deposition:

Electrochemical deposition was started with heating the prepared electrolyte solution to a desirable temperature (60°C). The power supply was adjusted to a suitable voltage. The produced current was recorded at a certain deposition time using stop watch. Then stirring the solution is directed to prevent bubbles aggregation on a cathode. The film thickness required was limited by deposition time. The deposition of gold nanofilms was performed at different period of time and constant temperature (60°C). Gold nanofilms with different thicknesses were deposited on silicon (100). Afterwards, the deposited electrode was removed from the cell and washed with double distilled water and dried with N_2.

Nano film thickness calculation:

The amount of gold deposited at the cathode and the amount dissolved at the anode are directly proportional to the product of the current and time (Faraday's law). The gravity method assisted by electrolyte calculation was used to calculate film thickness. In gravity method, material density ρ is represented by:

$\rho = m/ = m/A\ d$ .....(1)

Where m the deposited mass, V is the deposited volume, *A* is the deposited area and d is the film thickness.

The charge Q passed in period of time t:

$Q = I\ t$ .....(2)

Where I is the steady current of the deposition experiment.

Therefore the number of gold moles is equal to:

$I\ t/96320$ .....(3)

Where 96320 C/mol is coulomb per mole for electron.

If the gold valance number 3 is used, then:

Mass of deposited gold will be:

$I\ t\ 197/96320$ .....(4)

Where 197 is the atomic mass number in g/mole.

So the thickness is:

$d\ (cm) = [197/288960\ \rho\ A]\ I * t * = 211.8\ 10^{-5}\ I(A)$ .....(5)

Where t = 60 sec., ρ_{Au} =19.3 g/cm^3, *A* =1 cm^2.

$d(nm) = 21180 J(A/cm^2)$ .....(6)

Results and Discussion

Gold nano film thickness:

To set the deposition parameters according to the calculated experimental formula, we are considered to do the deposition at constant parameters .Now if the exposed silicon area (*A*) under electrolyte is equal to 1cm^2 and deposition time is 60 sec., so the thickness can be deduced from equation (7). The relation between film thicknesses- d (nm) as a function of current density J (A/m^2) for gold nanofilms is shown in Figure (1). The resulted linear data fitting formula is represented as follow:

$d(nm) = 2.12 * J(A/m^2)$ .....(7)

This is supposed to be an empirical formula deduce from the data fitting plot at fixed values of voltage (2.5 volt) and time (60 sec.), which is consequently used to calculate the thickness as a function of the current density.

Table (1)

Calculated current density as a function of gold film thickness at 60s and 1cm² sample area.

Thickness d (nm)	Current density J (A/m²)	Deposition rate (nm/sec)
5	2.4	0.083
10	4.7	0.160
20	9.4	0.330
30	14.2	0.200
50	23.5	0.830
100	47.2	1.660
150	70.8	2.500
200	94.3	3.300
250	117.9	4.160
300	141.5	5.000
350	165.1	5.830

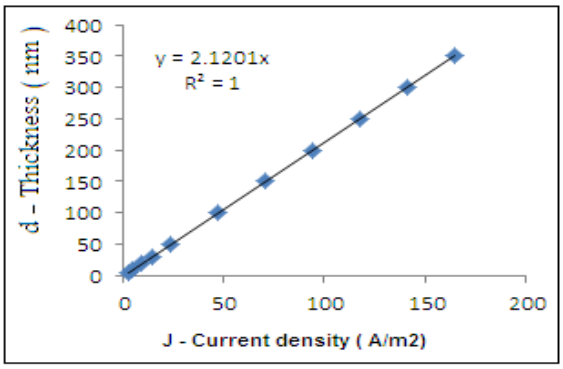

Fig. (1) Film thickness- d (nm) as a function of current density J (A/m²) for gold nanofilms.

Gold deposition rate:

The rate of electrodeposited gold on silicon was investigated relative to the current density which is shown in Table (1). Fig.(2) represents the deposition rate ranging from ≈ 5nm/min-40 nm/min, at required current deduced from the linear fitting formula as follows:

Deposition rate (nm/sec) = $3.522*10^{-2}*$ J (A/m²) .....(8)

The gold electrodeposition data listed in Table (1) was calculated using equation (8) and (9), one can estimate the thickness of gold required a specific current density. Suppose the plating process is operated at 2.4 A/m², so, the deposited of gold with an average thickness of 5nm and at 141 A/m² will be 300 nm and so on.

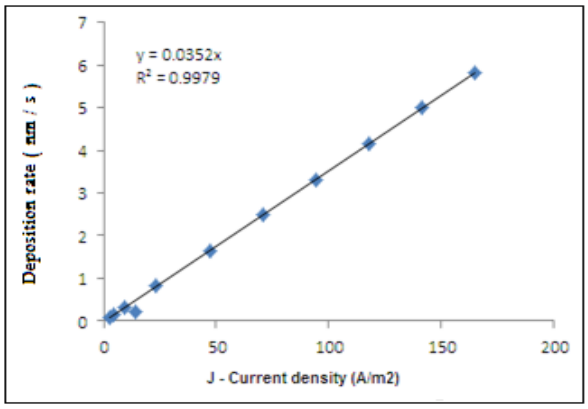

Fig.(2) Gold deposition rate as a function of current density.

XRD –Analysis

Gold sample electrodeposited on Si (100) was characterized by X-ray diffraction XRD. XRD–measurement was performed on a diffractometer (XRD-6000-Shimadzu Scientific Instrument–Japan). The structure determination of Au nanoparticles was carried out with an X-ray diffraction. X-ray tube of copper (CuK_α), working at V=40 KV, I= 30mA, scan range from 10-80 degree, and with step size 0.02 degree. Fig.(3) shows XRD analysis of gold film as deposited with thickness 170nm. This gold film revealed an amorphous structure. Fig.(4) shows crystalline structure for the same film (Fig. (3)) annealed at 600ºC for 1h with argon environment. In the XRD profile, four diffraction peaks can be indexed to FCC Au crystal. The XRD profile of the Au nanoparticles shows the intensity of a strong (111) diffraction peak, and the lower intensities of (200),(220) and (311) diffraction peaks are also seen. The extra high intensity strong peak is due to the silicon substrate. This suggests the growth of Au (111) orientation.

The domain size of the crystal can be estimated from the full width at half maximum (FWHM) of the peaks by means of the Scherrer formula, [23]

$D=K\lambda/\beta Cos\theta$ .....(9)

Where λ is the wavelength of the incident beam (λ = 0.15406 nm); β and θ are the corrected FWHM of the peak and the diffraction angle in radians respectively, and K= 0.94 is the Scherrer constant. The average crystalline size calculated was approximately 41.5 nm. Small crystalline nanoparticles for gold metal can successfully be produced using electrodeposition method which was characterized by X-ray diffraction.

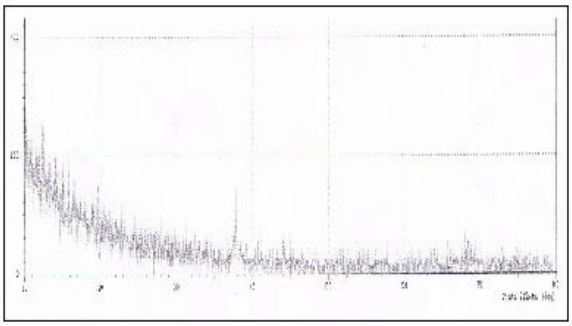

Fig.(3) X-ray diffraction profile for Au film (thickness 170nm) as deposited.

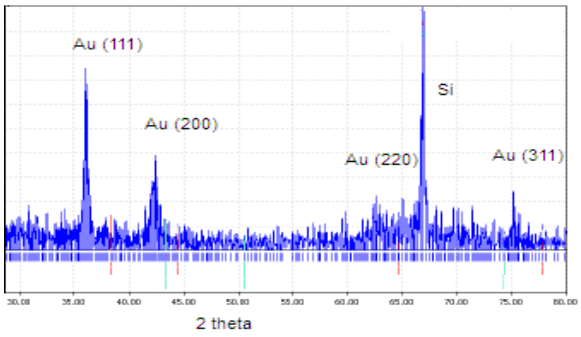

Fig.(4) X-ray diffraction profile for Au film(thickness (170nm) electrodeposited and annealed at 600°Cwith argon environment.

AFM Analysis:

Atomic force microscopy (AFM) was used as a good estimation tool for the shapes and sizes of the nanostructures. It is one of the most interesting analysis tools in the scanning probe microscope family (SPMs). AFM scanned the 3D to give a map of surface topography. This map allows the determination of different surface structure parameters. These are, the average height of the particles, the average roughness (S_a), and the root mean square (RMS) roughness (S_q).

Morphology of Au nanofilms

The surface morphology of Au films was analysed. An atomic force microscope (SPM - AA 3000 - Angstrom Advanced Inc.-USA) was used to observe the nanostructure of Au particales on silicon. The AFM system was operated in air by the tapping mode using silicon cantileaver. The images of 10μmx10μm area were obtained . According to the AFM observations, the surface roughness of the different silicon substrates is an important factor to form Au islands and nanopartical. High density of Au nanopartical could be deposited with a short deposition time. Fig.(5a) show 2D and 3D AFM (2μx2μ) images for 20 nm thickness chosen according to the formula (10) for gold electrodeposited on silicon (100) . The line section of the 2D image give the height of the film which is equal to 25nm. This value is closed to the film thickness. Fig. (5b) shows the distribution of the grain size , which is mostly ranging from 150nm-200nm

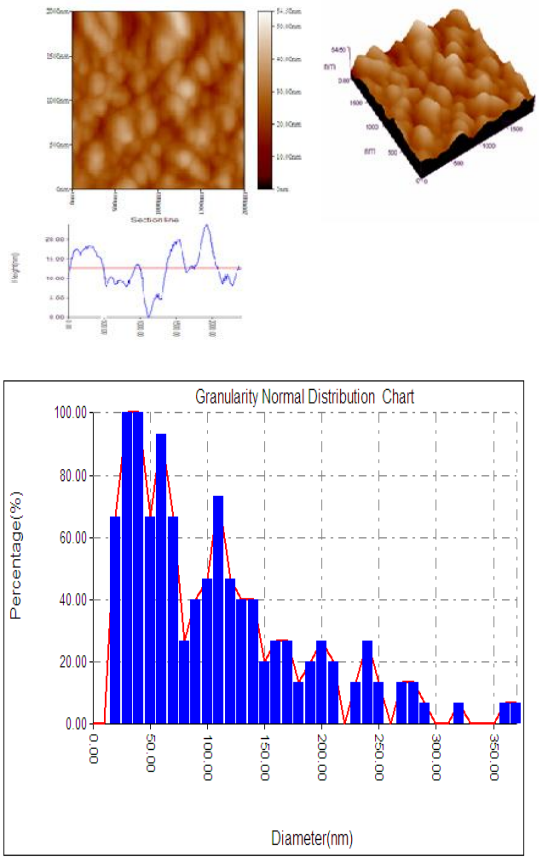

Fig.(5) 2D and 3D AFM (2μx2μ) images for 20 nm thick gold nanoparticles, as deposited.

Gold film was electrodeposited on silicon (100). The film was transferred into the middle of 1m, 2.6cm diameter quartz tube. The tube is a part of tube furnace. Fig.(6a) show AFM images in 2D and 3D for gold film with thickness of 80 nm, annealed at 600ºCfor 1h under argon gas to prevent film oxidation. This process shows Au film in the form of nanoparticles randomly distributed. The grain size distribution is mostly ranging from 50nm- 150nm as shown in Fig.(6b). After annealing at 600ºC for 1h, the film is slightly inhomogeneous shows the formation of coalescence of rounded nanoparticles like morphologies with some separation particles as show in AFM image. Table (2) is summarizing the AFM data analyzed for gold nanofilms.

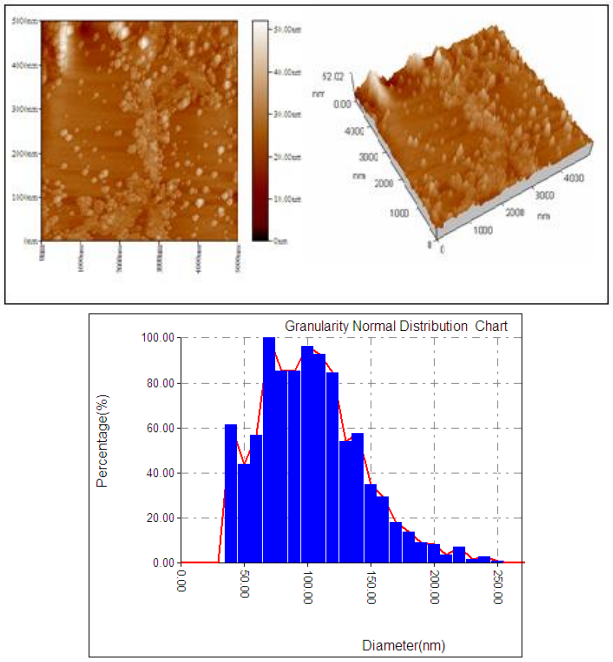

Fig.(6) AFM images in 2D and 3D for gold nanoparticles (film thickness= 80 nm) annealed at 600ºC /1h with argon gas.

Table (2)
AFM data for gold nanofilms electrodeposited on silicon (100).

Sample No./Fig.	*Film Thickness nm*	*Average roughness (S_a nm)*	*Surface RMS roughness (S_q nm)*	*Max. Partical Height (nm)*	*Average grain size (nm)*	*Treatment*
A1/ Fig.5	20	4.2	5.3	25	101	As deposited
A2/Fig.6	80	3	4.4	25	98	600°C/1h

Conclusion

In conclusion, this paper describes a simple, reproducible method to prepare gold nanostructure on silicon. Gold nanostructures were prepared by electrochemical method. We have optimized the electroplating conditions using a gold-sulfite electrolyte instead of the commonly used gold-cyanide which is by far less environment and operator friendly. Film thickness was successfully achieved experimentally which was confirmed by previous simple calculations. The product was characterized by XRD, and AFM. Gold nanoparticles were observed during the deposition process. X-ray diffraction peaks of gold electrodeposition showed predominantly Au (111) orientation, which is important for surface enhancement. The narrow (111) peak suggests that crystallite size at the dominant orientation is very large. These nanostructures could have promising applications to various sensors and electro catalytic.

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الخلاصة

تم دراسة التراكيب النانوية للذهب المرسب بالطريقة الكهربائية على قاعدة السليكون (100) باستعمال خلية مصنعة محليا. ان النتائج العملية لهذا البحث المتعلق بترسيب الذهب أستعملت محلول يستند على الكبريتات بدلا من سيانيد الذهب السام، اي ان المحلول المستعمل امن بيئيا. تم حساب سمك الغشاء كدالة لكثافة التيار ومعدل الترسيب باستعمال الطريقة الوزنية. حققت العلاقة المستنبطة سمك الغشاء المتوقع ترسيبه. تم الوصول الى معدل ترسيب بحدود 5- 40 نانومتر بالدقيقة. شخصت البنية البلورية لغشاء الذهب النانوي بواسطة حيود الاشعة السينية (XRD). تم فحص شكل غشاء الذهب المترسب بواسطة مجهر القوى الذرية (AFM). تبين ان شكل الغشاء الرقيق للذهب على السليكون ذو جسيمات بابعاد نانوية وذلك بعد اجراء عملية التلدين عند درجة حرارة 600 درجة مئوية.