# Corrosion of Gold Thin Films Deposited by Sputtering Deposition Method

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**Abstract**

Gold thin films have been prepared and deposited by sputtering deposition system at 17 nm and 34nm thickness on Ni-Cr-Mo alloy substrate. SEM, AFM, XRD, and Spectroscopic Reflectometer were used to characterize the thin films deposited. Electrochemical corrosion tests also have been carried out by measuring open circuit potential ($E_{o.c.p}$), Tafel extrapolation and cyclic polarization methods in artificial saliva solution at 37 $^0$C with elements analysis of the corrosion solution by using atomic absorption spectroscopy (AAS). The results obtained indicate the ability to deposit gold thin films (17nm and 34 nm ) by sputtering deposition method on Ni-Cr-Mo alloy with uniformity and without defects, decrease the roughness from 2.54 nm to 1.8 nm for gold nanocoated with 34nm and 17 nm respectively, FCC crystalline structure (111) with diffraction peaks results from XRD, and improvement of the localized corrosion resistance by decreasing the hysteresis loop of nanocoated with 34 nm of gold compared with the uncoated alloy.

**Keywords**: Corrosion, gold thin films, sputtering deposition method.

## تآكل اغشية الذهب الرقيقة المترسبة بطريقة التذرية

**الخلاصة**

تم تحضير وترسيب الاغشية الرقيقة من الذهب بطريقة التذرية عند سمك 17 نانومتر و34 نانومتر على سبائك ذات اساس نيكل –كروم- مولبدنيوم. تم استخدام المجهر الالكتروني الماسح و مجهر القوة الذرية و استخدام حيود الاشعة السينية و مقياس الانعكاسية الطيفية في تشخيص الاغشية المترسبة. واجريت اختبارات التاكل الكهروكيميائية بواسطة طريقة جهد الدائرة المفتوحة ومنحني تافل وطريقة الاستقطاب الحلقي كما تم تحليل سائل اللعاب الصناعي بعد التآكل بطريقة مطياف الامتصاص الذري. وبينت النتائج التي تم الحصول عليها امكانية ترسيب الاغشية الرقيقة من الذهب بطريقة التذرية على سبائك نيكل- كروم- مولبدنيوم بسمك 17 نانومتر و34 نانومتر مع تماثل الاغشية وخلوها من العيوب، تناقص الخشونة السطحية من 2.54 نانومتر الى 1.8 نانومتر بالنسبة للمطلي بسمك 34 و 17 نانومتر على التوالي، وكان



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التركيب البلوري ذات المكعب المتمركز الوجه بالاتجاه البلوري (111) مع نبضات نتجت من حيود الاشعة السينية، وتحسن مقاومة التآكل الموقعي من خلال تناقص منطقة التآكل الحلقي التنقري بالنسبة للمطلي بغشاء الذهب الرقيق بسمك 34 نانومتر مقارنة بالسبيكة غير المطلية.
**الكلمات المرشدة** : مقاومة التآكل ، اغشية الذهب الرقيقة ، طريقة الترسيب بالتذرية

## INTRODUCTION

Nanostructured thin films, deposited on substrates, play nowadays a quite significant role in various material science and technology applications due to their unique electrical and optical properties [1]. Most common applications are micro-electromechanical and nano-electromechanical systems, sensors, electronic textile, bioengineering, biomedical applications, generator of nonlinear optical properties, or devices for surface-enhanced Raman scattering. Ultrathin film of gold can be produced by various methods such as thermal evaporation [2], electrochemical deposition and electrodeposition[3-5]. Nanoparticles have been assembled by deposition using pulsed laser, electrochemistry, microwave, thermal heating of evaporated thin film [6-10], and electrochemical deposition [11]. Excellent properties of gold nanoparticles due to the small gold particles compared with the bulk materials. The ability to control the particles size and shape, and their surface conjugation with antibodies allows for both selective imaging and photo thermal killing of cancer cells due to their excellent biocompatibility and unique properties in surface plasma resonance, as an example in medical applications [12] . Increasing the corrosion resistance of implants alloys by coating the surface by thin films has another benefit which is biocompatible improvements [13]. Although alloys obtained in this way limit the metalosis phenomenon, (the migration of alloying elements into the tissues surrounding implant) and replacing the cytotoxic elements by biocompatible elements are under research.

Siegel *et al.* 2011 [14] studied the gold nanolayers sputtered with thicknesses 10 to 15 nm thickness on polytetrafluoroethylene (PTFE) surface and their changes induced by post deposition annealing at 100°C to 300°C and characterized by atomic force microscopy, zeta potential, and X-ray photoelectron spectroscopy (XPS). The results found significant carbon contamination, presence of oxidized structures on gold-coated observed in XPS spectra and decrease the surface roughness of gold coating. Maciej *et al.* 2012 [13] presented paper regards the research of the golden "nanocoatings" deposited on the plates made of zirconium oxide with coating thickness about 10 micron. The results found high quality of golden coatings with good tolerance of implanted materials with good biocompatibility. Dawood *et al.* 2013 [11] investigated the nanostructures of gold on silicon using electrochemical deposition method and used gravity method to calculate the film thickness as a function of current density and deposition rate. Anna 2013 *et al.* [1] induced the gold nanolayer and nanocluster coatings by heat treatment and evaporation technique on glass with (i) room temperature deposited, (ii) glass heated to 300°C, and (iii) the room temperature-deposited glass then annealed at 300°C. UV spectroscopy used to measure the optical properties of gold nanostructures with higher thickness deposited of 18 nm. The results found that the annealing process influences the structure and optical properties of gold films and the elevated temperature of glass during evaporation amplifies the peak of plasmon resonance in the structures, surface morphology being

significantly altered. Renyun 2014 *et al.* [15] reviewed porous gold films, provide a short review on the progress of porous gold films over the past ten years including the synthesis and applications of gold films.

The aim of this work is focusing on deposition of gold nanostructure thin films on the Ni-Cr-Mo alloy to produce homogenous and uniform films of gold then investigating the morphology and demonstrating the localized corrosion resistance of Au films deposited for medical implantation.

**Experimental Work**

Specimens of medical grade Ni-Cr-Mo alloy with dimensions of 10 x 10 $mm^2$ were used in this study. The surfaces prepared, cleaned by acetone ethanol and deionized water and then dried. The chemical composition of Ni-Cr-Mo alloy substrates shown in table (1).

**Table (1): Chemical composition of Ni-Cr alloy**

| Elements | Cr | Mo | Fe | Cu | Ni |
|---|---|---|---|---|---|
| Weight% | 20.9 | 9.94 | 2.4 | 0.13 | Bal. |

Targets of pure Au (99.995%) according to ISO 9001:2008 bought from Kurt J lesker company-USA were used in a magnetron sputtering deposition system type Kurt J lesker. System is calibrated with different targets and power and the calibration graph is used to estimate the power/time needed to deposit a given thickness of film. The deposition conditions were vacuum base pressure 2.8x10-7 Torr, rate of 2nm/min, Argon gas used at 20 standard cubic centimeter per minute (sscm), and pressure during deposition of 4 Torr. Scanning electron microscope (SEM) in the Ministry of Science and Technology–Baghdad used with an operating accelerating voltage of 3.5-10 kV in order to investigate the films deposition defects. Conductive carbon cement used to secure the samples on to specimen holders and smart SEM software used for controlling the imaging process. Surface roughness obtained by AFM (SPM Scanning Probe Microscope) in Nanotechnology center-University of Technology, Baghdad. The surface roughness of thin films deposited on glass is measured. Spectroscopic Reflectometer system type TFProobe, (Angstrom Sun Technology Inc., Germany) used in Ministry of Science and Technology–Baghdad, with software available for film thickness measurement of gold deposited on glass simultaneously with the Ni-Cr-Mo alloy substrates. X-ray Diffraction (XRD) type Philips (general electric diffraction Pw1840,2009) and made with Cu-Kα radiation at wavelength (λ =0.15418 nm), 40 Kv, 30 mA, scan axis 2θ range, started and end degree is (20-90 deg.), sampling step was 0.2º and speed at 3º / min. Electrochemical corrosion device used type WINKING M Lab 200 Potentiostat/ from Bank-Elektronik in Materials Eng. Dept./ University of Technology. Ni-Cr-Mo alloy is the working electrode, platinum electrode is the auxiliary electrode, and saturated calomel electrode (SCE) is the reference electrode. Electrochemical software with a potentiostat at a scan rate 0.5 $mA.sec^{-1}$ performed in electro-chemical measurements. Artificial saliva used in the test is shown in table (2).

**Table (2) Composition of artificial saliva [16,17].**

| Element | Conc.(g/l) |
|---|---|
| KCl | 0.4 |
| NaCl | 0.4 |
| $CaCl_2.2H_2O$ | 0.906 |
| $NaH_2PO_4.2H_2O$ | 0.69 |
| $Na_2S.9H_2O$ | 0.005 |
| Urea | 1 |

Open circuit potential ($E_{o.c.p.}$), Tafel extrapolation and cyclic polarization in artificial saliva solution at 37 ±1 $^oC$ were used. Corrosion potentials ($E_{corr.}$), corrosion current density ($i_{corr.}$), Tafel slops, breakdown potential ($E_{b.}$) and repassivation potential ($E_{rep.}$) are the main results obtained. Atomic absorption spectroscopy (AAS) in Ministry of Industry and Minerals / IBN SINA STATE COMPANY/ Baghdad used to study the elements analysis of the corrosion solution after corrosion test.

**Results and Discussion**

Fig. (1) shows SEM micrograph of the 34nm of gold film deposited on Ni-Cr-Mo alloy substrate after annealed at 300°C for 1h with argon environment. It can be observed that there isn't defect and the film is free-crack.

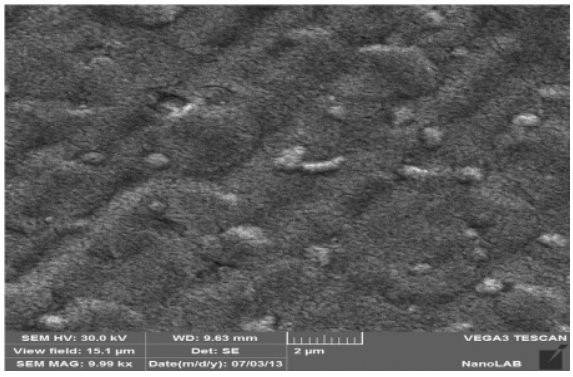



**Figure (1) SEM micrographs of 34nm of gold film.**

Fig. (2) shows AFM images of the nanocoated samples by thin films of gold. It seems that the morphology of gold thin film with different thicknesses was significant different with increasing the thickness of Au film, where the roughness decreases from 2.54 nm to the 1.8 nm as shown in Fig. (2). The increase of Au thickness leads to increase the smooth and homogenous of the layer and the globular structure being more pronounced

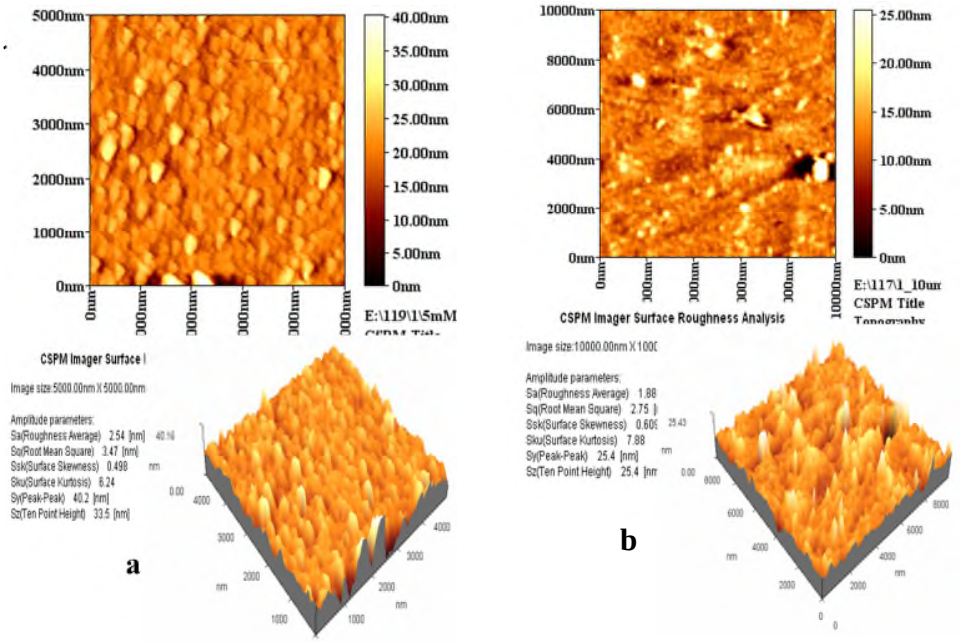



**Figure (2): AFM images results of gold films in two and three dimension; a) nanocoated with 17 nm , and b) nanocoated with 34 nm .**

Fig. (3) shows the XRD results of samples nanocoated with 34 nm of gold thin film and annealed at 300ºC for 1h with argon environment. Diffraction peaks can be indexed to FCC Au crystalline structure (111) according to CAS number 7440.57.5 determined from PCPDFWIN program as shown in table (3).

**Table (3): XRD results of Au thin film.**

| 2 Thete (deg) | d standard ($A^o$) | d measured ($A^o$) | hkl |
|---|---|---|---|
| 38.20 | 2.355 | 2.345 | 111 |
| 44.4 | 2.039 | 2.00 | 200 |
| 64.5 | 1.442 | 1.430 | 220 |
| 77.5 | 1.23 | 1.22 | 311 |
| 81.8 | 1.177 | 1.175 | 222 |

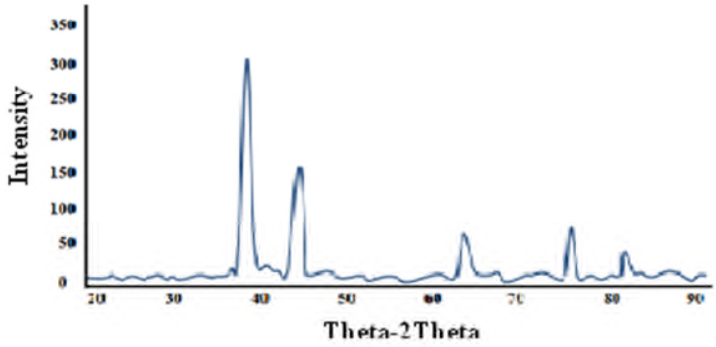



**Figure (3) XRD results of gold flim**

The average crystalline size calculated was 18.4 nm by Scherrer formula [18] which is;

$$D = \frac{K\lambda}{\beta Cos\theta} \qquad \ldots(1)$$

Where: λ is the X-ray wavelength of the incident beam (λ = 0.15406 nm); $\beta$ is the line broadening at half of the greatest intensity (FWHM) in radian, θ is the diffraction angle in radians too. K is the Scherrer constant (0.94).

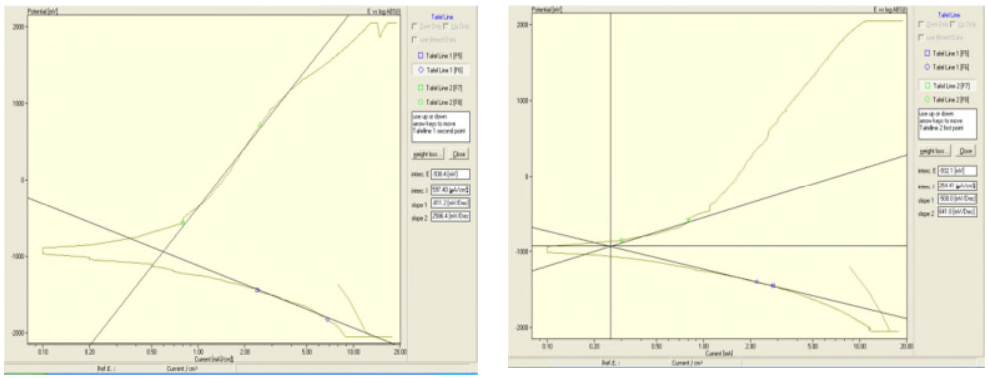
Figures (4 and 5) and table (4) show the electrochemical corrosion results ($E_{o.c.p.}$, $i_{corr.}$, $E_{corr.}$, $E_{b.}$, and $E_{rep.}$) for uncoated and nanocoated specimens by 34 nm thin films of gold in artificial saliva at 37 $^{o}$C. The $E_{o.c.p}$ of uncoated sample was (–675mV) and after nanocoated the $E_{o.c.p}$ changed to more noble number (-180 mV) which means more stability. Corrosion current densities ($i_{corr.}$) were 597.4 µA.cm$^{-2}$ and 254.41 µA. cm$^{-2}$ for uncoated sample and nanocoated with thin film of gold respectively.

**Table (4) electrochemical corrosion results.**

| Corrosion Parameters | Uncoated Ni-Cr-Mo alloy | Nanocoated with 34nm of Au |
|---|---|---|
| $E_{o.c.p}$ (mV) | - 675 | -180 |
| i corr (µA.cm$^{-2}$) | 597.4 | 254.41 |
| E corr (mV) | -938.4 | -932.1 |
| -a (mV/Dec.) | -811.2 | -500 |
| +b(mV/Dec.) | +2586.4 | +641 |
| $E_{b.}$(mV) | +2000 | +2000 |
| $E_{rep.}$( mV) | +1350 | No |

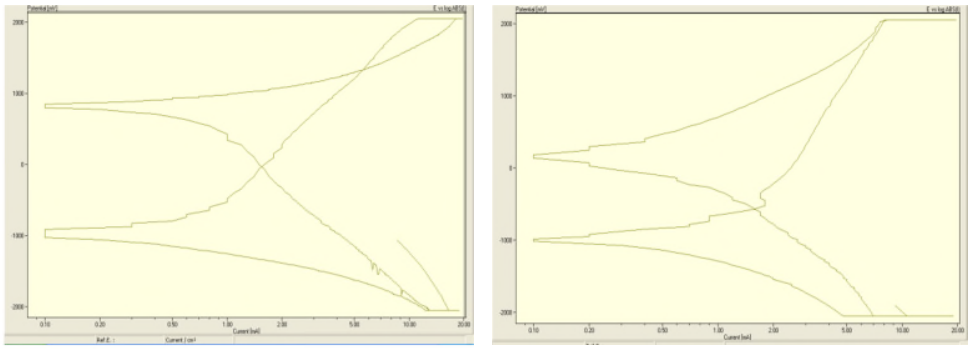
The more corrosion resistance of nanocoated samples by film is due to the stability of gold in the electrochemical corrosion reactions which leads to protect the surfaces from

the corrosion attacks. The $E_{corr.}$ of nanocoated samples is more than that of uncoated; it demonstrates the low tendency of gold film to the corrosion reaction. For localized corrosion analysis of active passive metals, is depended on $E_{b.}$ and $E_{rep.}$. Although the $E_{b.}$ of nanocoated and uncoated is equal (+2000 mV) but there isn't $E_{rep.}$ value of nanocoated with gold thin film compared with that of uncoated alloy, this means more localized corrosion resistance, no corrosion pits. Furthermore to the deceases the hysteresis loop of nanocoated samples with 34nm of gold compared with uncoated alloy as shown in the cyclic polarization results.



**a** **b**

**Figure (4 ): Tafel results of a) uncoated sample, b) nanocoated with 34 nm of gold.**



**a** **b**

**Figure (5): Cyclic polarization results of a) uncoated sample, b) nanocoated with 34 nm of gold.**

The element analysis result of metallic ions in artificial saliva by AAS for uncoated Ni-Cr-Mo alloy and nanocoated with 34 nm of Au after corrosion tests are tabulated in table (5). It is found that there are elements of Ni, Cr, and Mo in different concentrations for uncoated sample and no results found for nanocoated with 34 nm of gold.

**Table (5): AAS result after corrosion test.**

| | Account (ppm) | |
|---|---|---|
| **Element** | **Uncoated samples** | **Nanocoated with 34nm of Au.** |
| Ni | 0.018 | No results |
| Cr | 0.005 | |
| Mo | 0.260 | |

## Conclusion

Gold thin films can be deposited by using sputtering deposition method on Ni-Cr-Mo alloy with 17nm and 34nm with uniformity of the film and without defects. The roughness of the films decreases from 2.54 nm to 1.8 nm with increasing the film thickness from 17 nm to the 34 nm. The localized corrosion resistance of Ni-Cr-Mo alloy in artificial saliva at 37 $^{o}$C improved after deposition film of gold at 34 nm thickness, where there isn't $E_{rep.}$ value with decrease the hysteric loop compared with uncoated Ni-Cr-Mo alloy.

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## References

[1] Anna S., Petr S., and Irena K., "Gold nanolayer and nanocluster coatings induced by heat treatment and evaporation technique", Nanoscale Research Letters Vol. 8, No. 249, 2013.

[2] Piscopiello E., Tapfer L., and Antisari M., "Formation of epitaxial gold Nano islands on silicon (100)" Phys. Rev. Vol.78, No 3, pp.35305-35311, 2008.

[3] Gamero M., and Alonso C., "Deposition of nanostructured gold on n-doped Si-substrate by electrochemical methods", Journal of Applied Electrochemistry, Vol.40, No.1, pp.175-190, 2010.

[4] Xiao F., and Zeng Q., "Electrodeposition of gold nano-particles coatings from electrode/reverse micro emulsion system", Acta Physico-chemica sinica, Vol.23, No. 5, pp. 769-773, 2007.

[5] Jing F., Tong H., Kong L., and Wang C., "Electroless gold deposition on Si(100) wafer based on a seed layer of silver", Applied Physics A: Materials Science and Processing, Vol. 80, No. 3 , pp. 597 – 600, 2005.

[6] Donnelly T., and Krishnamurthy S., "Pulse laser deposition of nanoparticles film of gold", Applied Surface Science Vol. 254 pp.1303-1306, 2007.

[7] Fang J., You H., and Ding B.,"Large –area and high-density gold nano-particles arrays with sub-10nm gaps" Vol. 9, No. 9, pp. 2423 – 2427, 2007.

[8] Huang H., and Zhang S., "Microwave – assisted deposition of uniform thin gold film on glass surface" Vol. 200, No. 14-15, pp. 4389 – 4396, 2006.

[9] Hovel H., and Becker T., "Crystalline structure and orientation of gold clusters grown in preformed nanometer-sized pits", Applied Surface Science Vol. 115, No. 2, pp.124-127, 1997.
[10] Spadavecchia j., Prete P., and Lovergine N., "Au nanoparticles prepared by physical method on Si and sapphire substrates for biosensor applications" Vol. 109, No. 37, pp. 17347-17349 ,2005.
[11] Dawood A. Q., and Lafta S. H, "Investigation of Gold Nanostructures on Silicon Using Electrochemical Deposition Method", Journal of Al-Nahrain University Vol.16, No. 4, pp.134-140, 2013.
[12] Jakub S., Robert K., and Zdenka K., "Annealing of gold nanostructures sputtered on Polytetrafluoroethylene", Nanoscale Research Letters, Vol. 6, No. 588, pp. 1-6 ,2011.
[13] Maciej B., Maciej H., and Dariusz J., "Analysis of Ceramic Implants Surface with Golden Nano-Layer", J. of Metal Czech Republic, Vol. 2, No. 5, 2012.
[14] Kajzer W., Krauze A., Walke W., "Corrosion behavior of AISI 316L steel in artificial body fluids", Journal of Achievements in Materials and Manufacturing Engineering , Journal of Achievements in Materials and Manufacturing Engineering ,Vol. 31, No. 2 ,2008.
[15] Jakub Siegel, Robert Krajcar, Zdeňka Kolská, Vladimír Hnatowicz and Václav Švorčík1 "Annealing of gold nanostructures sputtered onPolytetrafluoro-ethylene" Nanoscale Research Letters j., Vol. 6, No.588, pp.1-6, 2011.
[16] Renyun Zhang * and Håkan Olin " Porous Gold Films—A Short Review on Recent Progress", Materials J., Vol. 7, pp. 3834-3854, 2014.
[17] Majed R. A., "Galvanic Corrosion of Dental Alloys and Amalgam in Artificial Saliva Containing Citric Acid", Eng. &Tech. Journal, Vol.31, Part (A), No.12, pp.2299-2310, 2013.
[18] B.D. Cullity, "Elements of X-Ray Diffraction" Adison-Wesley, 1978