International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/100206

The Effect of Annealing Temperature on the Structure and Hardness of Palladium Thin Film

Faezeh Ghaderi [1] , *Feridoun Samavat* [2] , *Majid Jafar Tafreshi*[1] *and Maryam Kiani* [2,*]

[1] Department of Physics, Semnan University, Semnan, Iran
[2] Department of Physics, Bu-Ali Sina University, Hamedan, Iran

Received: 21 Feb. 2021, Revised: 22 Mar. 2021, Accepted: 24 Mar. 2021
Published online: 1 May 2021.

Abstract: Palladium thin films, with a thickness of about 110 A, were deposited at room temperature on glass substrates, by electron beam evaporation method, and subsequently annealed at 523, 598, 673, 748, 773, 798 and 823 K for an hour, and then were cool down slowly. The structure and hardness of the thin films were investigated using X-Ray Diffraction (XRD) and Vickers Micro Hardness (MHV) analysis respectively. XRD patterns showed that the structure is amorphous before annealing and as the annealing temperature increases, the structure of Pd thin films become crystallized gradually. The Vickers Micro Hardness modifications of the Pd thin film showed that the heat treatment resulted in the structural compression of the sample and therefore the density increased compared to the preheating temperature. Thus, by heating up to the re-crystallization temperature, the Pd thin film-tensile strength increased, which is itself due to the mechanical behaviour of the material, and has a significant effect on its efficiency. So we realized that the hardness of the thin films is directly affected by annealing temperature.

Keywords: Pd thin film; Electron Beam Evaporation; Physical properties; Mechanical properties; X-Ray Diffraction (XRD); Vickers Micro Hardness (MHV); Annealing temperature, PVD deposition; Nanoparticles; Crystallization; re-crystallization.

1 Introduction

In methods of layer deposition, when a substance is broken down from a bulk-form into its constituent atoms, molecules, or ions, are deposited on a substrate, a film is constructed which is hence called a layer. This film, in turn, bestows a number of characteristics namely electrical, mechanical, and other physical properties upon the substrate, such that the overall collection of the substrate's properties are enhanced in some manner or way [1, 2]; thus, in recent years, the science of thin films, especially that of thin metallic films which enhance optical, electronic, magnetic and catalytic traits of some materials with sub-micron clusters, has seen serious amount of growth, and much research has been conducted in the aforementioned field [3-9]. The properties of thin films usually differ to that of bulk traits of matter. Given the fact that the surface energy of nano-particles is higher than that of bulk materials, their surface activity is, therefore, greater to that of bulk substances, which will usually result in nano-particles, particularly metal nanoparticles and metal oxides, have powerful inductance and catalytic traits, and can be utilized as nano-catalysts in various settings [10]. Due to their high surface activity, nano-catalysts increase both the efficiency and the speed of chemical reactions [11, 12]. Electrical conductance diminishes as the layer gets thinner, and the band gap energy, alongside both electrical and special resistances, increase in the process [13, 14]; moreover, the electrical resistance of layers usually increases as the temperature rises [15]. With the layers becoming thinner, their magnetization effect diminishes [16], and their optical absorption intensifies [17]. Due to the increase in the surface to volume ratio in thin films, the chemical and thermal reaction of the aforementioned materials is greater than the bulk counterparts [18]. The breach of corrosive substances into the structure of nanoparticles is mainly hard, due to the fact that these nano-materials have a high contact surface area. Also, nano-particles empower the ionic and hydrolytic resistance by increasing physical and chemical bonds of the surface, hence, reducing breakability. With respect to the use and properties of thin layers, one can simply use these materials to augment technologies like solar cells and optical sensors, most of which are involved in electrical and ferro-electrical engineering practices [19, 20].

*Corresponding author E-mail: kiani1331@gmail.com

Palladium is a rare metal with a melting point of 1826.9 K, which has an FCC structure and is considered an n-type semiconductor material [6,7]. This metallic element is solid in room temperature and becomes highly malleable when exposed to enough heat. Warm palladium (temperature at 333 K and pressure at 1 atm) can fascinatingly increase hydrogen absorption up to 900 times its volume [21], and it is for this reason that it is utilized in gas refineries, switching equipment in telecommunications, and also aerospace engineering [22]. Also, since palladium has a high absorption and transformation rate, and boasts a wide energy band gap, it has attracted much attention from the materials science society [6, 23-25]. By using porous nano-layers of palladium in hydrogen separating membranes, and also in electrochemical sensors, one can benefit from the high efficiency of surface adsorption and reaction cross sections of palladium particles with respect to the creation of PdHx in the presence of hydrogen, which would entail the separation of hydrogen from other gases, and the reduction of oxygen presence [25-29]. Given the above, it is common to use thin palladium layers and its alloys in many studies spanning from the likes of being a cathode catalyst in fuel cells, and existing in gas sensors and hydrogen-selection membranes, in which palladium is quite essential [22, 25-28, 30].

Thin film depositions are generally divided into two main categories; these are physical and chemical depositions [19]. Physical vapour deposition is one of the simplest and most cost-effective methods of layer deposition, and is very versatile in its use [35-37]. Also, this method does not produce environmentally harmful by products in the very least [38, 39]. Electron beam vapour deposition method is one of the many methods of physical vapour deposition, that can be employed for substances with high melting points; furthermore, this method ensures a much higher level of purity for the layers when compared with other applicable ones [40]. Some of the methods utilized in creating palladium thin films includes, RF sputtering method [41], Chemical vapour deposition [42], Electro-deposition [43], Immersion Plating [44], deposition via Precipitation [45], Electro-chemical deposition [46], Chemical bath deposition [47]. In this investigation, we have produced palladium thin film via the electron beam deposition method, and have subsequently studied the effects of temperature annealing on the structure and physical properties, such as its micro-hardness, of the said substance via XRD analysis and Micro-Vickers Hardness tests.

2 Experimental Sections

In order to get rid of all the substrates of pollution, the mentioned materials were placed in an ultrasonic cleaning device for more than 10 minutes, and were then relocated into a container containing acetone, which was finally rinsed off with distilled water, and dried with an air blow-drier. The prepared substrates were then placed into the electron beam layer deposition device, and once the pressure reached 〖10〗^(-8) bars, the layer deposition of palladium on the glass substrate occurred with a rate of 1/5 (Å/s). The resultant thin palladium films were 110 Å thick and were then baked for 1 hour at temperatures of 523, 598, 673, 748, 773, 798 and 823 K respectively.

XRD analysis was carried out via the AP2000 device with a Cu-Kα emission with a wavelength 1.54 Å on all samples within a 20 to 90-degree range. The hardness tests were conducted via the micro-Vickers hardness tester device of ILLINOIS 60044, using a pin made of tungsten carbide and a 0.49 N, with each marking lasting around 15 seconds.

3 Results and Discussion

3.1 XRD Analysis

The thin films were deposited on glass substrates of similar thickness and were baked in different temperatures, then they were analysed via the X-ray diffraction method. The diffraction spectrum of X-rays is portrayed in Figure 1, which shows the effects of heating on the crystals of the palladium thin films.

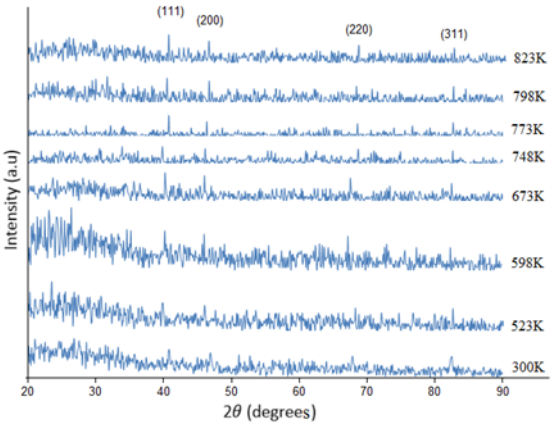

Fig. 1: X-ray diffraction patterns of Pd thin film according to annealing temperatures.

The intensity of diffracted rays in the amorphous matter is wide, yet in the crystalline matter is takes the form of sharp peaks; therefore, the wide and spread out peaks displayed in Figure1 show that the palladium thin films possess an amorphous structure in room temperature. When heat treatment is applied, the samples are mainly amorphous up to around 523 K, but when the temperature is increased above that threshold, the intensity of sharp peaks in the diffraction spectrum grows, and the wideness of the peaks decreases, and the intensity of ambient peaks and valleys falls in an evident manner. Given that the presence of these peaks is evidence to the fact that the heat treatment process creates crystalline seeds, it could be understood that further increases in the temperature (up to about 773 K) could

trigger a re-crystallization reaction in the sample which would result in the layers adopting a crystalline structure to themselves. The main plane direction of the formed nano-particles is parallel to (111), (200), (311), (222). Using Eq.1, which is known as the Debye-Scherer equation, and with the help of a software called X-POWDER, the size of the particles has been calculated.

$$t = \frac{0.9\lambda}{B\cos\theta_B} \quad (1)$$

In this formula, t is the size of the particles, λ is the wavelength of the X-rays, B is the Full Width at Half Maximum of the peaks, and θ is the Bragg angle of the peak caused by the diffraction. The effect of thermal treatment on XRD data of palladium thin film is collected in Table 1. The variations in the size of the largest nanoparticles of gold and palladium were plotted by annealing temperature can be seen in Figure 2.

Table 1: The effect of thermal treatment on XRD data of thin palladium layers.

Annealing Temperature (K)	d-spacing (Å)	Grain Size (nm)	(hkl)
523	2.2548	11	(111)
	1.9688	13	(200)
598	2.2369	8	(111)
	1.9688	9	(200)
673	2.2369	39	(111)
	1.9661	17	(200)
748	2.2548	42	(111)
	1.9581	75	(200)
773	2.2159	62	(111)
	1.9607	89	(200)
798	2.2229	9	(111)
	1.9397	25	(200)
823	2.2264	18	(111)

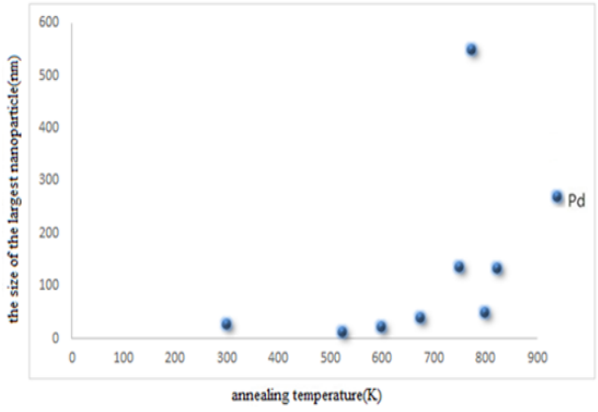

Fig.2: Changes in the size of the largest nanoparticles of palladium according to annealing temperature.

The data of Table 1 and Figure 2 show that by increasing the temperature of the annealing and baking sequence, the intensity of main peaks and the size of the nano-particles grow, and the width of the peaks diminishes, which is mainly due to the growth of crystals in the structure; thus, it shows that the increase in temperature in the annealing process has significant effects on the creation of a crystalline structure within the layers, and on the crystal layers themselves as well. With respect to the effects of heat treatment on the width of the main peaks, and also regarding the increase in the intensity of the peaks in crystalline phase, which shows the volume of the crystals that are created in this process, it can be concluded that the transition from amorphous structure to crystalline structure has occurred slowly and smoothly; furthermore, the size of palladium nano-particles in a temperature of around 773 K has reached its zenith, and the ambient peaks and valleys have hit their record low. Since the intensity of the diffracted spectrum of X-rays are dependent upon the growth of particles and the empty spaces within the surface [48], the increase in the intensity of the main peaks and the decrease in the ambient ripples at around **773 K are mainly due to the atoms being situated around** their equilibrium positions, the surface defects, and the occurrence of a re-crystallization in this temperature.

By taking into account the position of the main peaks, and the spacing between the crystal layers in the X-ray diffraction pattern of a substance, one can find the tensions within that substance. Hence, if, before the tension is applied, the distance between crystal layers of the substance is d_0, and the position of the main peak is at 2θ, after applying the tension the distances should be greater or less than d_0, and the main peak positioning should differ to that of the initial 2θ [49]. Thus, by paying heed to the fact that the positioning of the main peaks and the d-spacing of the crystalline layers has not differed too much, one can conclude that the palladium thin film have not been subjected to any form of tension.

The results of a similar investigation on palladium conducted by another group of researchers has shown that by increasing the temperature, the intensity of the absorbed peaks in the X-ray diffraction spectrum of palladium thin films has been amplified, and their width has been reduced; moreover, the creation of crystallites, and the diameter of the nanoparticles have been augmented by the increase in the temperature. In other words, by increasing the annealing temperature, one can increase the size of the nanoparticles [1], which is in complaisance with our current findings.

3.2 Vickers Micro-Hardness

One of the most important measurable mechanical properties in metallic samples is the hardness of that sample. Hardness test by the Vickers method is the most

common form of the aforementioned tests in measuring the resistance of metals, which is done by observing the diameter of the marks made by a pin that incorporates a certain amount of force [50]. The average hardness of the sample palladium films in various temperatures has been presented in Table 2.

Table 2. Roughness level (Ra) of Pd thin film through of the 2, 5 & 10μm windows in terms of annealing temperature.

Annealing temperature(K)	Average of the Vickers micro hardness(HV)
Without annealing	611
748	556
823	740

The heat treatment process has three stages in general, which are, recovery, re-crystallization and seed growth. In the re-crystallization stage, the seeds that have been malformed are replaced by a series of flawless seeds. This process is usually accompanied by a reduction in the hardness and toughness of the substance, as well as an increase in its malleability. The change in micro-hardness of palladium thin films with respect to annealing temperature can be seen in Figure 3.

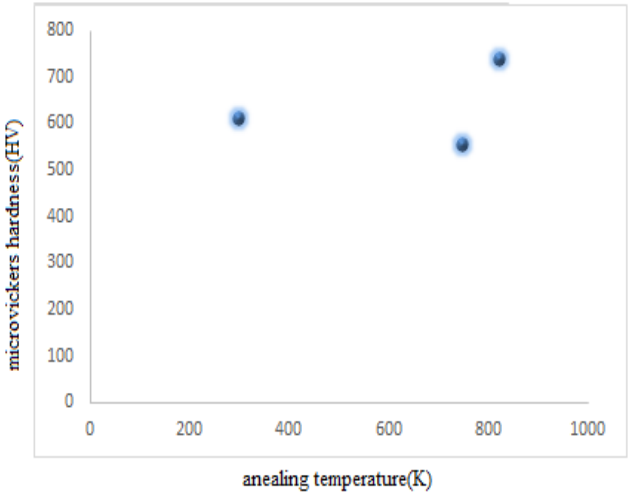

Fig. 3: Changes in average of Vickers micro hardness values of Pd samples in terms of annealing temperature.

The change in the hardness of the palladium thin films is negligible so far because the amorphous structure of the substance is intact. In truth is, before the temperature has reached the re-crystallization threshold, the sample experiences an increase in hardness, yet above such temperatures, the sample begins to lose its hardness. The hardness of palladium samples before re-crystallization is similar to that of the process mentioned above, and in temperatures of around 823 K, the amount of hardness reported by the Vickers test is 184HV higher than the previous measurements done in the temperature of 784 K, and is subsequently the highest for this investigation. The changes in micro-hardness show that the palladium thin films become denser after the heat treatment process; thus, one of the possible reasons associated with the increase of hardness in thin films annealed at high temperatures could be the changes of structural density that they face in this process.

4 Conclusions

In summary, palladium thin films were deposited on a glass substrate via the electron beam vapour deposition method. The results of the diffraction analysis of X-rays have shown us that the structure of the samples before the heat treatment process is amorphous, but by increasing the temperature, the crystalline structure overpowers the amorphous structure. The main direction of the nano-particles is parallel to the plane directions of (111), (222), (200), and (311). With an increase in temperature, the intensity of the main peaks are amplified, and the crystalline structure in that plane becomes even more augmented. The results of Vickers hardness tests show that by increasing the temperature in the heat treatment process before reaching the re-crystallization threshold, the hardness of the samples increases, and after that, by increasing the temperature, even more layers assume a more crystalline form, and with that, the hardness of the samples diminishes.

References

[1] F. Samavat, P. Taravati Ahmad, F. Mahmoodi, M. Samavat, M. Tavakoli,The effect of annealing on the size and morphology of palladium nanoparticles. Am J Cond Mat Phys., **2(3)**, 73-6, 2012.

[2] Q. Fang, G. He, W.P. Cai, J.Y. Zhang, W. Boyd, Palladium nanoparticles on silicon by photo-reduction using 172 nm excimer UV lamps. Applied Surface Science., 226 **(1-3)**, 7-11,2004.

[3] Z. Novotna, A. Reznickova, L. Viererblova, J. Kolafa, Z. Kolska, J. Riha, V. Svorcik, "Novotna, Z., Reznickova, A., Viererblova, L., Kolafa, J., Kolska, Z., Riha, J., & Svorcik, V., Physicochemical properties of gold nanostructures deposited on glass. Journal of Nanomaterials., 1-8, 2014.

[4] A. Schaub, P. Slepicka, I. Kasparkova, P. Malinsky, A. Mackova, V. Svorcik, "Gold nanolayer and nanocluster coatings induced by heat treatment and evaporation technique", Nanoscale Research Letters, 8 (2013) 249–256.. Gates, Why word is used, *Microsoft Lett..*, **69 (5)**, 53-60, 1998.

[5] C. Feng, L. Guo, Z. Shen, J. Gong, X.Y. Li, C. Liu, Sh. Yang,. Synthesis of short palladium nanoparticle chains and their application in catalysis. Solid state sciences., **10(10)**, 1327-1332, 2008.

[6] K.R. Patil, Y.K. Hwang, M.J. Kim, J.S. Chang, S.E. Park,

Patil, Preparation of thin films comprising palladium nanoparticles by a solid–liquid interface reaction technique. Journal of colloid and interface science., **276(2)**, 333-338, 2004.

[7] F. Samavat, F. Mahmoodi, P. Taravati Ahmad, M. Samavat, M. Tavakoli, S. Hadidchi, Effect of annealing temperature on the optical properties of palladium thin film.", Physical Chemistry., **2**, 103-106, 2012.

[8] U. Kreibig, M. Vollmer, Optical properties of metal clusters (Vol. 25). Springer Science & Business Media., 2013.

[9] J.B. PelÇka, W. Paszkowicz, P. Dluzewski, M. Brust, C.J. Kiely, M. Knapp, E. Czerwosz, "Characterisation of thin films containing Au and Pd nanoparticles by grazing-incidence X-ray diffraction and related methods. Journal of alloys and compounds., **328(1-2)**, 248-252, 2001.

[10] V. Polshettiwar, R.S. Varma, Green chemistry by nano-catalysis. Green Chemistry., **12(5)**, 743-754, 2010.

[11] N. Sharma, H. Ojha, A. Bharadwaj, D.P. Pathak, R.K. Sharma, "Preparation and catalytic applications of nanomaterials: a review", RSC Advances., **5(66)**, 53381–53403, 2015.

[12] S. Chaturvedi, P.N. Dave, N.K. Shah, "Applications of nano-catalyst in new era", Journal of Saudi Chemical Society., **16(3)**, 307–325. 2012.

[13] A. GHaderi, S.M. Elahi, S. Solaymani, M. Naseri, M. Ahmadirad, S. Bahrami, A.E. KHalili, Thickness dependence of the structural and electrical properties of ZnO thermal-evaporated thin films. Pramana., **77(6)**, 1171-1178, 2011.

[14] A.C. Hasiao, M.E. McHenry, D.E. Laughlin, M.R. Tomaria, V.G. Harris, Magnetic properties and crystallization kinetics of a Mn-doped FINEMET precursor amorphous alloy. IEEE transactions on magnetics., **37(4)**, 2236-2238.

[15] F. Lacy, Developing a theoretical relationship between electrical resistivity, temperature, and film thickness for conductors. Nanoscale research letters, **6(1)**, 1-14, 2011.

[16] V. Hari Babu, J. Rajeswari, S. Venkatesh, G. Markandeyulu, "Effect of thickness on structural and magnetic properties in nanocrystalline Fe-N thin films", Journal of Magnetism and Magnetic Materials., **339** ,1-5, 2013.

[17] N.E. Makori, I.A. Amatalo, P.M. Karimi, W.K. Njoroge, "Optical and Electrical Properties of SnSe Thin Films for Solar Cell Applications", American Journal of Condensed Matter Physics., **4(5)** , 87-90, 2014.

[18] B. Tlili, C. Nouveau, M.J. Walock, M. Nasri, T. Ghrib, "Effect of layer thickness on thermal properties of multilayer thin films produced by PVD", Elsevier., **86 (8)**, 1048-1056, 2012.

[19] L. Zhang, F. Ying, W. Wu, P.C. Hiberty, S. Shaik, "Topology of Electron Charge Density for Chemical Bonds from Valence Bond Theory: A Probe of Bonding Types", Chemistry - A European Journal., **15(12)**, 2979–2989, 2009.

[20] Y.R. Reddy, "An Introduction to Thin Films", Department of physics, Kalkatiya Government College, Warangal, Indi., 1-20, 2010.

[21] The Editors of Encyclopeadia Britannica, "palladium (Pd): Chemica Element", Encyclopedia Britannica, Retrieved 16 May 2014.

[22] W. Sun, A. Hsu, R. Chen, "Palladium-coated manganese dioxide catalysts for oxygen reduction reaction in alkaline media", Journal of power sources., **196 (10)**, 4491-4498, 2011.

[23] E. Kowalska, E. Czerwosz, J. Radomska, "The Methods of Synthesis of Nanopores Carbon-Palladium Materials", Electronics., **1** , 32-35,2009.

[24] C. Benvenuti, P. Chiggiato, F. Cicoira, Y. L'Aminot, V. Ruzinov, "Vacuum Properties of Palladium Thin Film Coatings", Vacuum., **73 (2)**, 139-144, 2004.

[25] X. Wei, T. Wei, H. Xiao, Y. S. Lin, "Nano-Structured Pd-Long Period Fiber Gratings Integrated Optical Sensor for Hydrogen Detection", Sensors and Actuators B: Chemical., **134(2)**, 687-693.2008.

[26] Z. Ke, G. Huiyuan, R. Zebao, L. Yuesheng, L. Yongdan, "Preparation of Thin Palladium Composite Membranes and Application to Hydrogen/ Nitrogen Separation", the Chinese Journal of Chemical Engineering., **15(5)**, 643-647,2007.

[27] D. Zalvidea, A. Diez, J.L. Cruz, M.V. Andres, "Hydrogen Sensor Based On a Palladium-Coated Fiber-Taper With Improved Time-Response", Sensors and Actuator B., **114 (1)**, 268-274.2006.

[28] C.L. Tien, H.W. Chen, W.F. Liu, S. Jyu, S.W. Lin, Y.S. Lin, "Hydrogen Sensor Based on Side-Polished Fiber Bragg Gratings Coated With Thin Palladium Film", Thin Solid Films., **516(16)**, 5360-5363,2008.

[29] X. Luo, A. Morrin, A.J. Killard, M.R. Smyth, "Nanoparticles in Electrochemical Biosensors", National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland., **19(501)**, 473-501. American Scientific Publishers, 2011.

[30] K. Zhang, H.Y. Gao, Z.B. Rui, Y.S. Lin, Y. D. Li, "Preparation of Thin Palladium Composite Membranes and Application to Hydrogen/Nitrogen Separation", Chinese Journal of Chemical Engineering., **15 (5)**, 643-647.2007.

[31] W.E. Vargas, I. Rojas, D.E. Azofeifa, N. Clark, "Optical and electrical properties of hydride palladium thin films studied by an inversion approach from transmittance measurements", Thin Solid Films., **496(2)**, 189-196, 2006.

[32] N. Atta, M. Kady, A. Galal, "Palladium nanoclusters- coated polyfuran as a novel sensor for catecholamine neurotransmitters and paracetamol", Sensors and Actuator B., **141 (2)**, 566-574. 2009.

[33] L.A. Kibler, M. Kleinert, V. Lazarescu, D.M. Kolb, "Initial stages of palladium deposition on Au (hkl) Part III: Pd on Au(110)", Surface Science., **498 (1-2)**, 175–185, 2002.

[34] G.A. Somorjai,Y. Li, Introduction to surface chemistry and catalysis. John Wiley & Sons, 2010.

[35] A. Wagendristel, Y. Wang, "An Introduction of Physics and Technology of Thin Films", World scientific, 1994.

[36] Y.K. Mishra, S. Mohapatra, D. Kabiraj, A. Tripathi, J.C Pivin, D.K. Avasthi, "Growth of Au nanostructures by annealing electron beam evaporated thin films", Journal of

optics a: Pure and applied., **9 (9)**, S410–S414,2007.

[37] S. Behrens, W. Habicht, K. Wagner, E. Unger, "Assembly of Nanoparticle Ring Structures Based on Protein Templates", Advanced Materials., **18 (3)**, 284-289, 2006.

[38] Z. Liu, R. Levicky, "Formation of nanoparticle rings on heterogeneous soft surfaces", Nanotechnology., **15(11)**, 1483-1488, 2004.

[39] Y. Sun, Y. Xia, "Triangular Nanoplates of Silver Synthesis, Characterization, and Use as Sacrificial Templates For Generating Triangular Nanorings of Gold", Advanced Materials., **15(9)**, 695-699,2003.

[40] Milton Ohering, "Materials Science of Thin Films, Deposition and Structure", 2nd Edition, New York, Academic Press., 2002.

[41] S. Öztürk1, N. Kılınç, "Pd thin films on flexible substrate for hydrogen sensor", Journal of Alloys and Compounds., 674, 179-184.

[42] A. Niklewski, T. Strunskus, G.Witte, C. Woll, "Metal-Organic Chemical Vapor Deposition of Palladium: Spectroscopic Study of Cyclopentadienyl-ally", Chem. Mater., **17(4),** 861-868, 2005.

[43] B.A.F. Previdello, E. Sibert, M. Maret, Y. Soldo-Olivier, Palladium Electrodeposition onto Pt (100): Two-Layer Underpotential Deposition. Langmuir., **33(9),** 2087-2095,2017.

[44] J.E. Philpott, B.s, Immersion plating of palladium. Platinum Metals Review., **6(2)**, 144-146.1962.

[45] G. Scheen, M. Bassu, A. Douchamps, C. Zhang, M. Debliquy L.A Francis, "Palladium nanoparticle deposition via precipitation: a new method to functionalize macroporous silicon", Science and Technology of Advanced Materials., **15(16)**, 065002 (11pp), 2014

[46] A. Sahin, Q. Huang, J.M. Cotte, B.C. Baker-O'Neal, "Electrochemical Palladium Deposition for Reducing Critical Dimensions in Nanostructures", Journal of The Electrochemical Society., **161(12)**, D697-D703,2014.

[47] N. A. Shah, A. Nazir, W. Mahmood, W.A.A. Syed, S. Butt, Z. Ali, A. Maqsood, "Physical Properties and Characterization of Ag Doped CdS Thin Films", Journal of Alloys and Compounds., **512 (1)**, 27- 32,2012.

[48] C.M. Muller, R. Spolenak, "Microstructure evolution during dewetting in thin Au films", Acta Materialia., **58 (18)**, 6035-6045.2010.

[49] B. Bhushan, O. Marti, "Scanning Probe Microscopy-Principle of Operation, Instrumentation, and Probes, Nanotribology and Nanomechanics", Springer., 33-93, 2011.

[50] X.F. Pan, H. Zhang, Z.F. Zhang, M. Stoica, G. He, J. Eckert, "Vickers hardness and compressive properties of bulk metallic glasses and nanostructure-dendrite composites", Journal of Materials Research., **20(10)**, 2632–2638, 2005.