Effect of laser Fluence Energy on Morphological, Structural and Optical Properties of Gold and Silver Thin Films Prepared by Pulse Laser Deposition Method

The 5th International Scientific Conference for Nanotechnology and Advanced Materials and Their Applications ICNAMA 2015 (3-4) Nov.2015

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ABSTRACT

We report the growth and characterization of (Ag, Au) nanoparticles thin films deposition on a glass substrate by pulse laser deposition (PLD) method. The (Ag, Au) thin films prepared through different laser fluence (0.4, 0.6 and 0.7) J/cm^2. The effect of laser fluence energy on the morphological, structural and optical properties were studied by XRD, AFM and UV-Visible spectrophotometer.

X-ray diffraction showed nanostructure, with dominated peak at 2θ values 38.3182° corresponding to (111) for silver and peak observed at 2θ values 38.2° which can be indexed to the (111) of face-centered cubic (fcc) structure for Au. Surface topography studied by atomic force microscopy revealed narrowed size distributions, with grain sizes ranging from 21.81 to 37.06 nm for Ag, and grain sizes ranging from 12.63 to 15.01nm for Au thin films. The results showed the Average gran Size increased with increasing laser fluence energy and RMS roughness increased with increasing laser fluence energy. Optical properties measurements showed that(Ag, Au) thin films have two peak the first one related with interband transitions, and the second peak formation of a surface plasmon peak (SPR). Optical properties measurements showed transformation from metallic properties of bulk (Ag, Au) to semiconductor properties when formed by sort of nanostructure evidenced by the formation of optical energy gap about (0.8, 0.7 and 0.5) eV when laser fluence increased (0.4, 0.6 and 0.7) J/cm^2 respectively for Ag thin films. when grain size become smaller the optical energy gap increased. Optical energy gap(E_g) decreased (1.4, 1.2 and 0.8) eV when laser fluence increased (0.4, 0.6 and 0.7) J/cm^2 respectively for Au thin films.

Keywords: Physical thin film synthesis, Nano-Structured metal, Pulse Laser Deposition of Gold and Silver.

تأثير كثافة طاقة الليزر على المورفولوجيا و التركيب و الخصائص البصرية للأغشية الرقيقة للذهب والفضة المحضرة بطريقة الترسيب بالليزر النبضي

الخلاصة

تمت دراسة النمو و الخصائص لأغشية (Ag,Au) النانوية المرسبة على ركائز زجاجية بطريقة الترسيب باستخدام الليزر النبضي (PLD). اغشية (Ag,Au) الرقيقة حضرت باستخدام كثافة طاقة ليزر مختلفة J/cm2 (0.4, 0.6 and 0.7) . تأثير كثافة طاقة الليزر على المورفولوجيا والتركيب والخصائص البصرية تمت دراستها باستخدام XRD, AFM and UV-Visible spectrophotometer .حيود الاشعة السينية اظهر التراكيب النانوية، وكانت اعلى قمة عند الزاوية 2θ التي قيمتها °38.3182 المطابقة ل(111) للفضة، ، و اعلى قمة عند الزاوية 2θ التي قيمتها °38. 2المطابقة ل(111) للذهب المتمركز الاوجه. طوبوغرافية السطح درست باستخدام مجهر القوة الذرية حيث كشف ان حجم التوزيع سوف يتضيق والحجم الحبيبي يتراوح من 21.81nm الى 37.06 nm لأغشية الفضة، والحجم الحبيبي يتراوح من 12.63nm الى 15.01nm لأغشية الذهب. النتائج اضهرت ان معدل الحجم الحبيبي يزداد بزيادة كثافة طاقة الليزر و خشونة السطح تزداد بزيادة كثافة طاقة الليزر. قياسات الخواص البصرية الامتصاصية بينت ان الاغشية الرقيقة للفضة والذهب تمتلك قمتين الاولى تعود الى الانتقالات بين حزم الطاقة الداخلية ، والثانية تعود الى التردد الرنيني للبلازمون (SPR). قياسات الخواص البصرية بينت تحول خواص المادة من خواص المعدن الى خواص اشباه الموصلات وان الاغشية تمتلك فجوة طاقة بصرية تقلeV (0.8, 0.7 and 0.5) بزيادة كثافة طاقة الليزرJ/cm^2 (0.4, 0.6 and 0.7) للأغشية الرقيقة للفضة. عندما يقل الحجم الحبيبي للمادة النانوية فان فجوة الطاقة البصرية تزداد. فجوة الطاقة البصرية تقلeV (1.4, 1.2 and 0.8) بزيادة كثافة طاقة الليزرJ/cm^2 (0.4, 0.6 and 0.7) للأغشية الرقيقة للذهب.

INTRODUCTION

Pulsed laser deposition is defined as a promising technique for deposition of metals thin films [1]. Pulsed laser deposition is for many reasons a versatile , controllable method for producing thin films of materials[2]. Pulsed laser deposition technique is popular in the research community for the deposition of thin film due to numerous advantages, including low contamination level, high deposition rate and stoichiometry of the target is preserved in the deposited films[3]**.** The idea of PLD is simple. A pulsed laser beam is focused onto the surface of a solid target. The absorption of the electromagnetic radiation by the solid surface leads to rapid evaporation of the target materials. The evaporated materials consist of highly excited ionized species. They presented themselves as a glowing plasma plume immediately in front of the target surface if the ablation is carried out in vacuum [4]**.**

Metals (Ag, Au, etc.) nanoparticles supported on solid substrates or embedded in solid thin films are of great interest owing to their unique physical and chemical properties [5,6], which enable applications such as synthesis of composite materials for nonlinear optical devices [7,8], and catalysts [9]. For the optical applications, the light-induced localized surface plasmon resonance (SPR) is the main optical property to control, which in turn depends on the size, size distribution, shape, and dielectric properties of the metallic nanoparticles, as well as their surrounding dielectric medium [10]**.**

The fundamental laser emission of Nd:YAG laser is at 1064 nm. The fundamental emission of Nd:YAG can be frequency doubled to 532 nm wavelength using a suitable nonlinear optical crystal at the cost of nearly half the laser energy at fundamental[11]. The ablation rate is strongly influenced by the characteristics of the laser beam (pulse duration, number of pulses, energy, fluence, wavelength) [12- 16]

processed material (mass density, surface reflectivity, optical absorption, thermal conductance) and by ambient conditions [12,14,17,18].

Experiment procedure

To prepare nanoparticles thin films, the PLD system used, consists of the main parts shown in figure (1) vacuum chamber, Q- switched Nd:YAG Laser**,** lens **,** quartz window, pressure monitoring**,** rotary pump and diffusion pump. To preparation nanoparticles thin films the vacuum chamber was cleaned by acetone**.** The glass slides Put on a slides holder so that it is against the target on the rotated target holder and the distance between the target and the slides is 3cm. The Nd:YAG Laser radiation is focused by lens on the surface a rotated target at the incident angle of approximately 45°. Nd:YAG Laser spot size (1.5)mm. All valves of vacuum chamber closed, and start the process of creating a vacuum. Vacuum pumps works to empty the system from air mixture Initially rotary pump creates a vacuum of ~10^{-3} mbar, when the diffusion pump becomes operational and can create a vacuum up to ~10^{-5} mbar**.**

The substrate heated to (300 ^{o}C) by using halogen lamp to improve the adhesion of deposited material**.** After reaching the desired vacuum, vacuum chamber valve must open and generate laser pulses plasma column that contains nanoparticles which are deposited on the substrate. The PLD thin films were analyzed by XRD, AFM and UV-Visible spectrophotometer.

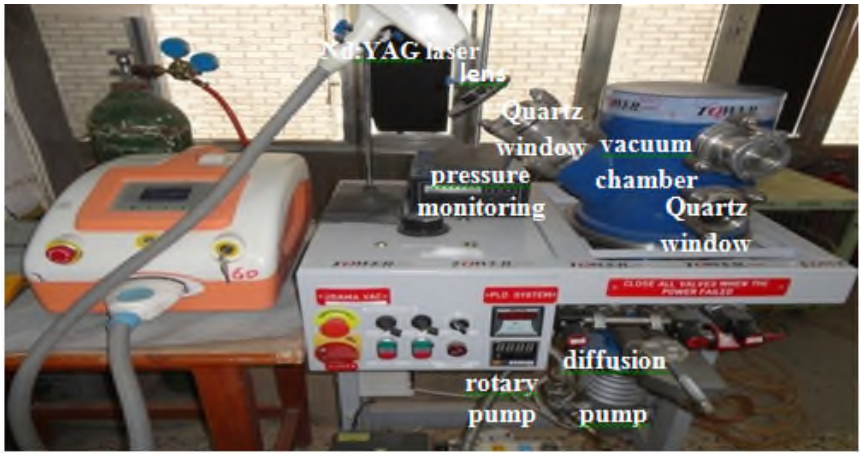
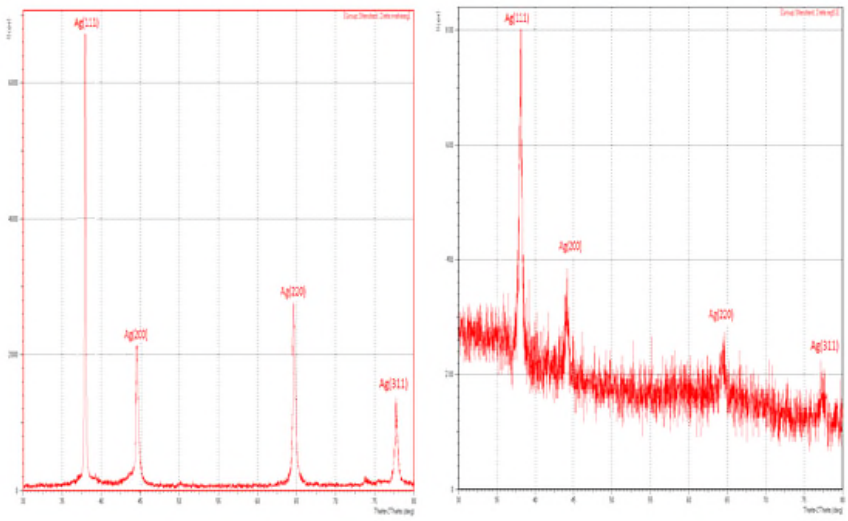


Figure (1) PLD system Set-Up

Results and discussion

XRD peaks of (Ag, Au) films deposited on the glass substrate at laser fluence energy 0.7 J/cm^2 vacuum chamber pressure (10^{-5}) mbar, and substrate temperatures 300^{o}C. The XRD patterns of silver nanoparticles thin film shown in the figure (2). Peaks at 2 θ values of 38.3182^{o}, 44.4975^{o}, 64.6119^{o} and 77.5385^{o} corresponding to (111), (200), (220) and (311) planes respectively of silver is observed and compared with the standard powder diffraction card (JCPDS: 04–0783)[19]. The peak intensity for (111) is found 800 counts per second for samples irradiated at 0.7 J/cm^2, 1064 nm peaks at 2θ values of 38.3182 ^{o} . Whereas the grain size approaching to maximum 33.981nm at (311). The grain size of silver nanopartical thin film was shown in Table (1) .

The typical XRD pattern of Au film show in figure (3). XRD pattern of Au nanoparticles have four peaks observed at 2θ values 38.2°, 44.4°, 64.576°, and 77.547° which can be indexed to the (111), (200), (220), and (311) reflections respectively of face-centered cubic (fcc) structure of Au, respectively. (JCPDS: 04-0784), shows the pure crystalline nature of the prepared particles. The intensity of (111) diffractions is 860 for the prepared sample. Thin film is highly oriented in the (111) direction, the XRD pattern displays all the characteristic diffraction peaks of polycrystalline Au This is similar to the result obtained by the researcher Irissou *et. al.* [20]. Indicating that the faces of these nanoparticles are primarily composed of (111) planes[21]. The grain size of gold nanoparticles thin film is shown in Table (2).

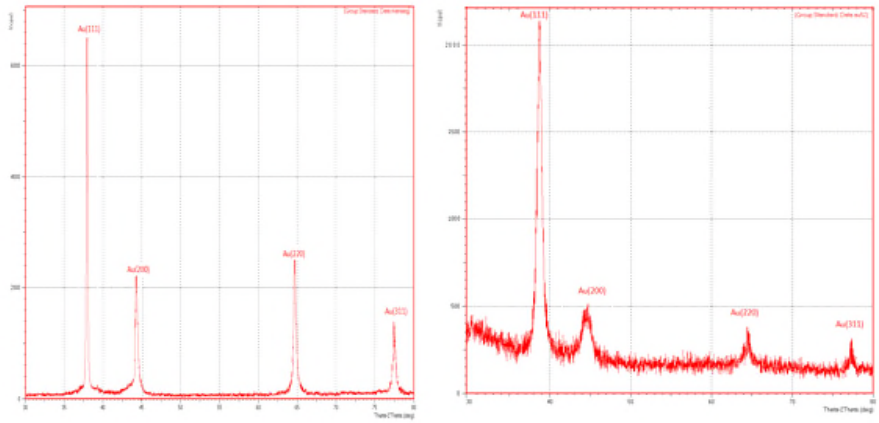


(a) (b)

Figure (2) X-Ray diffraction for Ag (a) Ag target before ablation (b) Ag thin film.

Table(1) X-Ray diffraction for Ag thin film

2θ Degree	(h k l)	FWHM (β)	Grain size nm
38.3182	(111)	$8.726646*10^{-3}$	16.82023645
44.4975	(200)	$17.453292*10^{-3}$	8.572005256
64.6119	(220)	$8.726646*10^{-3}$	18.76797254
77.5385	(311)	$8.726646*10^{-3}$	20.33635026



(a) (b)

Figure (3) X-Ray diffraction for Au (a) Au target before ablation (b) Au thin film.

Table (2) X-Ray diffraction for Au thin film

2θ Degree	(h k l)	FWHM Degree β	Grain size nm
38.2	(111)	$17.453292*10^{-3}$	8.406703158
44.4	(200)	$34.906585*10^{-3}$	4.0290050273
64 .576	(220)	$34.906585*10^{-3}$	4.698684587
77.547	(311)	$34.906585*10^{-3}$	5.094924852

The AFM images of thin films deposited on glass substrate and at substrate temperatures 300^{o}C, vacuum chamber pressure (10^{-5}) mbar, different laser fluence energy (0.4, 0.6 and 0.7) J/cm^{2}. Figure (4) and Table (3) show the grain sizes of Ag thin films between (21.81-37.06) nm and the RMS roughness between (1.24 -3.42) nm. This difference is considered large, however, the possibility that two or more thin layers of silver nanoparticles are formed. AFM showed that at 300^{o}C deposition temperature Ag islands grow in height and diameter and the number of island decreases. This behavior is similar and agreement to the result obtained by Ranjbar *et. al.*[22]and Al-Kinany *et.al.*[23].

The film deposited shows clearly the presence of larger Ag nanoparticles with a broad distribution in size and shape this indicating coalescence between small islands. Figure (5) and Table (4) shows the grain size of Au thin films between (12.63-15.01)nm and the RMS roughness between (0. 45- 0. 676) nm. It can be clearly seen from the figures that when increasing in the laser fluence, the grains size increases. This is attributed to the two types of formation, the first one is the increase of laser fluence energy ablation large grains, and the second is attributed to the possibility of some small grains agglomerated to form greater grains. This leads to an increase in the roughness and grain size diameter.

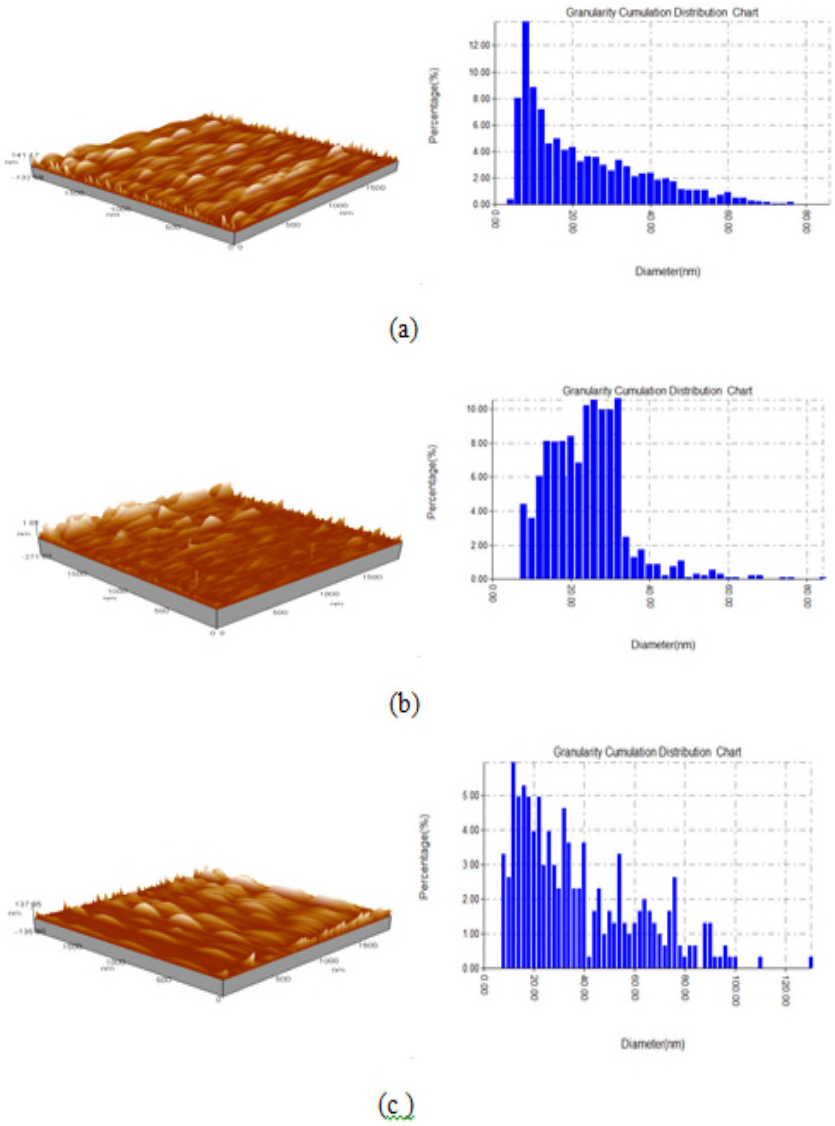


Figure (4) AFM images of Silver films deposited on glass substrate at vacuum chamber pressure 10^{-5} mbar, and substrate temperature(300ºC)at different Laser fluence: (a) 0.4 J/cm^2 (b) 0.6 J/cm^2 (c) 0.7J/cm^2.

Table (3) AFM parameter for Ag at different laser fluence

Sample	Fluence [J/cm^2]	Grain size [nm]	RMS roughness [nm]
Ag	0.4	21.81	1.24
	0.6	34.89	2.03
	0.7	37.06	3.42

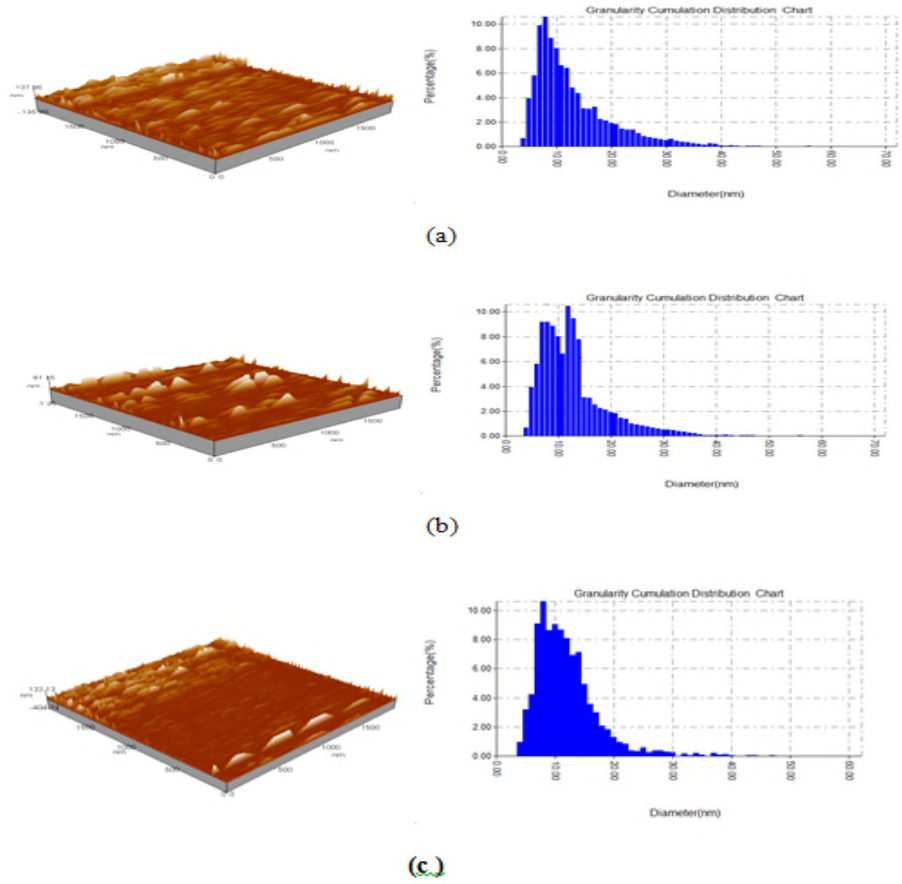


Figure (5) AFM images of gold films deposited on glass substrate at vacuum chamber pressure 10^{-5} mbar, and substrate temperature(300ºC)at different Laser fluence: (a) 0.4 J/cm^2 (b) 0.6 J/cm^2 (c) 0.7 J/cm^2.

Table (4) AFM parameter for Au at different laser fluence

Sample	Fluence [J/cm^2]	Grain size [nm]	RMS roughness [nm]
Au	0.4	12.63	0.45
	0.6	13.67	0.63
	0.7	15.01	0.676

It can be seen that absorption of Ag thin films increases when the laser fluence increase. Figure (6) shows absorbance spectrum of Ag thin films, which is have two peak the first one at (346 nm) related with interband transitions, and the second peak at (600 nm) formation of a plasmon band peaked . The expected surface plasmon resonance (SPR) peak increases in amplitude and shifts to the longer wavelength. This behavior is similar and agreement to the result obtained by J.C. Alonso *et. al.* [24] and Al-Kinany *et.al.*[23].

Figure (7) shows absorbance spectrum of Au thin films, which is related with interband transitions of metallic gold, and formation of a plasmon band peaked at 600

nm. This is similar to the result obtained by the researcher Lu *et. al.*[25]. A characteristic peak of absorbance near 600 nm grew progressively by increasing laser fluence energy. Size effects may shift the plasmon resonance to longer wavelength values when the cluster size is increased. The physical and chemical properties of nanomaterials depend on the particle size [26].

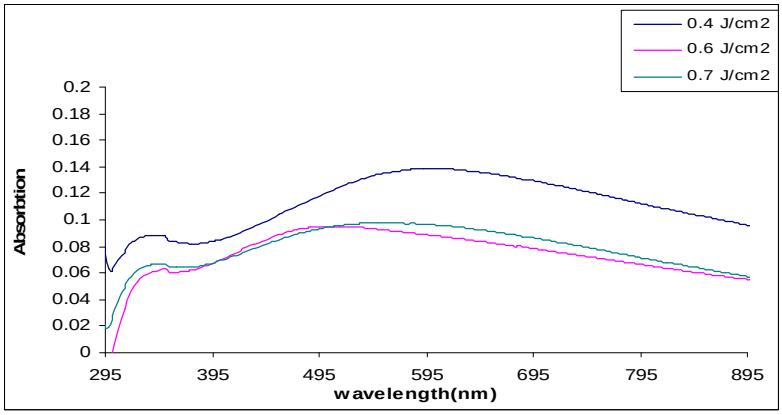


Figure (6) Absorbance spectrum of nanostructure Ag thin films at different laser fluence (0.4, 0.6 and 0.7) J/cm^2.

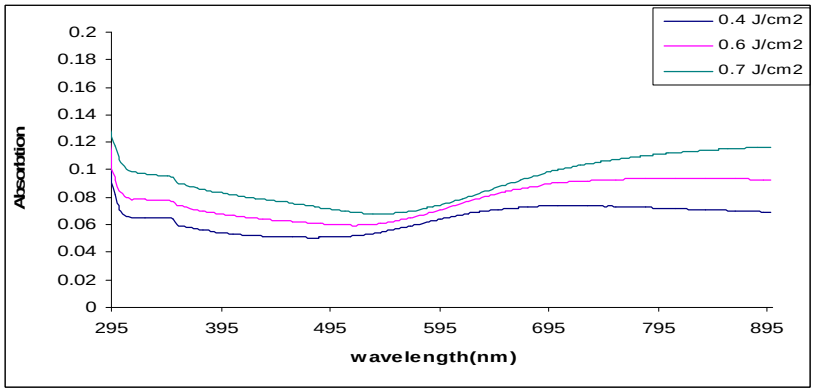


Figure (7) Absorbance spectrum of nanostructure Au thin films at different laser fluence (0.4, 0.6 and 0.7) J/cm^2.

The metals gold and silver in the bulk state does not have energy gap and energy levels are overlapping, but at the nano thin-film properties of the material will be changed, turning gold and silver metals to semiconductors and have energy gap. The optical energy gap decreased when the laser fluence energy increased . when the laser fluence energy increased the grain size increased. The decrease of energy gap is attributed to the increase of grain size and disorder in the material, which means allowing excitation secondary levels inside the energy gap leads to decreasing the width gap.

Figure (8) shows optical energy gap (E_g) for Ag thin films. The optical energy gap decreased to (0.8, 0.7 and 0.5) eV when laser fluence increased (0.4, 0.6 and 0.7) J/cm^2 respectively.

Figure (9) shows energy gap (E_g) for Au thin films. Optical energy gap(E_g) decreased (1.4, 1.2 and 0.8) eV when laser fluence increased (0.4, 0.6 and 0.7) J/cm^2 respectively.

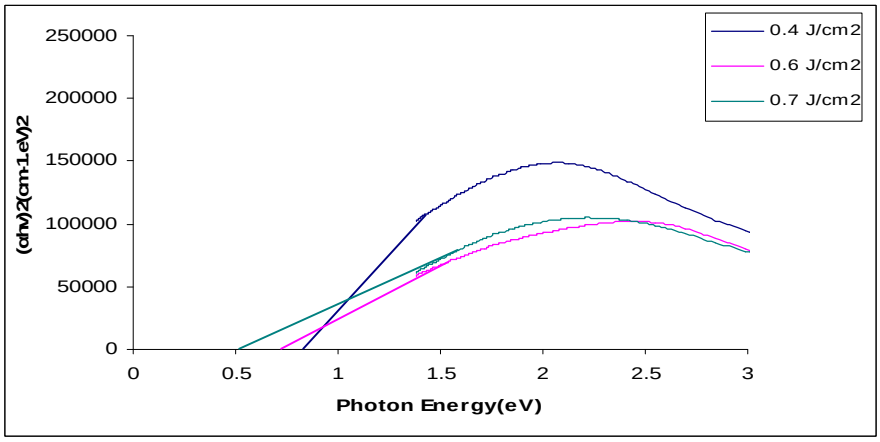


Figure (8) Energy gap of Ag thin films at different laser fluence (0.4, 0.6 and 0.7) J/cm^2.

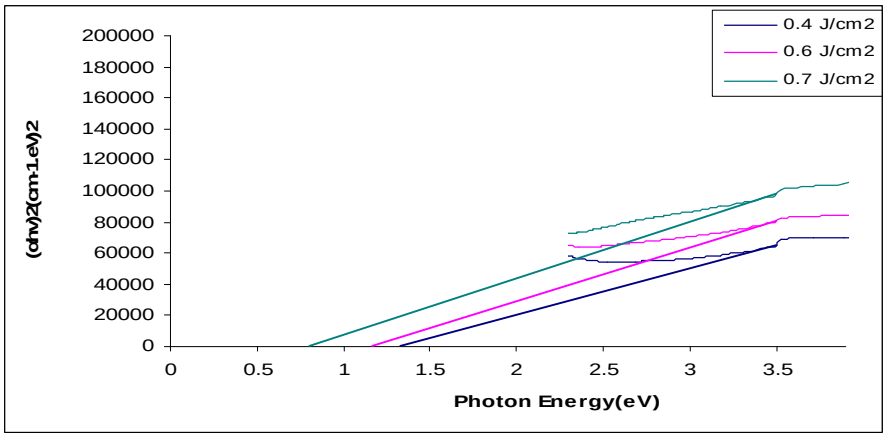


Figure (9) Energy gap of Au thin films at different pulses energy (60, 80 and 100)mJ.

CONCLUSION

1-The results ensured that Ag and Au thin films prepared by PLD are Nanoparticles.
2-X-ray diffraction patterns shows that Ag and Au thin films are polycrystalline.
3-AFM images indicate that the grain size and Roughness of the nanoparticles observed at the surface depended on the laser fluence energy.
4- The results indicate the grain size and Roughness of the nanoparticles thin film increased with increasing laser fluence energy.
5- Our results indicate the absorption with increasing of laser fluence energy.
6-The value of energy gap decreased with increasing of laser fluence energy.

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