Studying the effect of the number of laser pulses on the structure, morphology, and optical properties for a thin film of GO-Ag nanocomposites

Mousa Muhammad Ali Al-Mousawi 1, Amer Al-Nafiey 2*, Ghaleb Al-Dahesh 3.
1,2,3 University of Babylon / College of Sciences for Women \ Department of Laser Physics / Iraq
* amer76z@yahoo.com

Abstract: In this paper, studying the effect of the different numbers of laser pulses on graphene oxide -silver nanoparticles (GO-Ag NPs) thin film prepared by the pulse laser deposition (PLD) on silicon and quartz substrates. The laser using in PLD is an ND-YAG laser with a wavelength (1064 nm)m with a repetition rate of 6 Hz with a laser pulse duration (9 ns). Atomic force microscopy AFM and XRD using for analysis of the thin film, the results showed the possibility of preparing thin films with different sizes of granule and crystalline sizes on the nanoscale. Also, show that the granular size and crystal size of the nanoparticles decrease with the increase in the number of laser pulses with the constant energy. Moreover, the optical properties measurements showed that the absorbance and absorption coefficient increase with the increase in the number of pulses when the energy is constant, while the energy gap decreases with increasing the number of pulses These results were promises to producing the thin film for Graphene oxide- silver nanocomposites for different applications compatible with it.

Keywords: number of laser pulses, PLD, GO-AgNPs

1. Introduction

Nanotechnology has been considered an interdisciplinary field of physics, chemistry, and materials science concerned with the design, manufacture, and application of nanomaterials. This branch of science aims to understand the basic physical and chemical properties of nanomaterials and nanostructures, and due to the variety and novelty of the application of nanomaterials in electronics, medicine, and various other fields of application [1,2], the science of nanomaterials developed accordingly and became at the forefront of applied research interests [3].

Among the most famous of these nanomaterials is graphene and graphene oxide, where the graphene is a nanomaterial has tremendous interests due to its distinctive properties that arise from being a flat monolayer of carbon atoms (graphite) which are two-dimensional (2D) in the shape of a honeycomb and the most important characteristics of graphene are its large surface area, high chemical stability, strong mechanical strength, and unique electrical and electronic conductivity properties [6,5,4].

Graphene oxide is a chemical compound composed of carbon, oxygen, and hydrogen in variable proportions. Graphene oxide (GO) can be Obtaining by the modified Hummer method but retains many of the valuable properties of pure graphene, which is easier and cheaper. Moreover, it is easy to deal with because of the presence of oxygen in the composition, which causes a great attraction for the growth of chemical structures on its surface [8]. Graphene and GO are an important way to stabilize inorganic nanoparticles, as it can increase the fixation of metal nanoparticles on graphene sheets as a new method.
for developing composite materials [7]. For that, to improve the properties of graphene oxide, nanomaterials such as silver nanoparticles (Ag NPs) can be doped or decorated on the graphene oxide sheets to form the (GO-Ag NPs) where the silver nanoparticles possess excellent properties such as optical, electrical, and biological that are very important for different applications [9].

There are several methods for preparing the nanomaterials, including the PLD method, which is considered one of the best, cheapest and simplest techniques for the deposition of semiconductors, metals, and their oxides in different conditions. From its first use in 1960 [10], is possible to obtain high-purity films and high deposition rates and obtain films of different thicknesses by controlling the number of pulses as indicated by previous studies [11, 13-12]. So, many reports preparing graphene oxide and its applications [14-15] and preparing the (GO-Ag NPs) compound by other methods moreover, the pulse laser ablation can be used to prepared GO-Ag NPs [17,16] that indicated the possibility of using pulse laser to formation this film by controlling the conditions.

In this study, the (PLD) method will be used to prepared (GO-Ag NPS) thin film on quartz slides and study the structural, morphology, and optical properties of this compound.

2. The Experimental part

Graphene oxide has been prepared by the Hummer's Method and according to the previous study [18]. For preparing the thin film of GO-Ag NPs on the quartz and silicon substrate, first, we cleaning the substrates with ethanol and distilled water to remove the impurity, then depositing a thin layer of graphene oxide on them by the drop cast method. For depositing silver nanoparticles on the substrate by Pulse Laser Deposition (PLD) in the Advanced Materials Research Laboratory in the Department of Laser Physics at the College of Sciences for Women - University of Babylon.

The PLD consists of, vacuum chamber and laser system, the vacuum chamber have a pressure of 2.5 x 10-3 m bar to avoid the oxidizing of target materials. The laser system parameters for the Q-switched Nd: YAG model, are the wavelength of the first Harmonic oscillator 1064 nm, pulse energy (10-1000) mJ, repetition frequency (1-10) Hz, and laser pulse duration (9 ns), for that we choose the number of pulses to be (200,300,400,500) for samples (S1, S2, S3, S4) respectively with pulse energy (180 mJ), repetition frequency 6 Hz, and laser pulse duration 9 ns.

To study the crystal structure and morphology we used X-ray diffraction and atomic force microscopy (AFM), and ultraviolet (UV) spectroscopy used to measure the absorbance, absorption coefficient, and optical energy gap of the thin film for the GO-Ag NPs

3. RESULTS AND DISCUSSION

1. X-ray diffraction (XRD) results

The X-ray diffraction results showed three main peaks representing Diffraction planes of of silver nanostructure at angles 2θ (38°, 44°, 64°), which correspond to the planes (111), (200), (220) respectively, as the results showed an increase in intensity when increasing the number of pulses according to the following figures (1,2) This indicates that there is a high increase of degree of crystallinity (with a change in crystallite size from (42.457nm) to (21.767 nm) by increasing the number of laser pulses and with constant energy and as shown in the tables (1) below, this corresponds to the JCPDS (file no: 89-3722) found to possess an fcc structure.

The crystallite size calculated using the Scherrer’s equation

\[ G = \frac{k \lambda}{B \cos \theta} \]

Where \( \lambda \) represents the wavelength of (0.15406 nm) X-rays, \( \theta \) represents the Bragg (diffraction) angle, \( G \) represents the crystalline size, and \( B \) represents the full width at half maximum (FWHM) in units of
radial angles. Figures (1,2,3,4) showed the appearance of other peaks due to impurities such as silver oxide and silver carbonate (which were formed due to the high temperature of heating substrate inside the vacuum chamber) and some of them are due to graphene oxide and the reduced graphene oxide[13]. The stronger planes indicate silver as a major constituent in the sample.

![Figure 1: X-ray diffraction of sample S1 - GO-Ag NPS thin film](image1)

![Figure 2: X-ray diffraction of sample S2 - GO-Ag NPS thin film](image2)

![Figure 3: X-ray diffraction of sample S3 - GO-Ag NPS thin film](image3)

![Figure 4: X-ray diffraction of sample S4 - GO-Ag NPS thin film](image4)
2. AFM Results

The presence of atomic force microscopy (AFM) examinations as in Figures (5,6,7,8) below also includes a surface smooth and high-quality adhesion to silicon bases, in addition to the formation of semi-spherical clusters with close grain sizes (fine grains). The increase the number of laser pulses, as shown in Table (2), we note a decrease in the grain size with a general decrease in surface roughness. Due to that during the deposition process is the growth of the thin film layers through the interaction of the ablation products inside the plasma and Which leads to a purification of the grain size by the occurrence of secondary laser ablation with an increase in the pulses number, and this in turn led to a decrease in the grain size. The fragments of high energies represent the ions, and the uncharged fragments determine their velocity due to the multiplicity of collisions with the charged particles led to appears a coalescences as in fig.(8) [13].

![Figure (5): AFM image of S1 sample at 200 pulses](image-url)
Figure (6): AFM image of S2 sample at 300 pulses

Figure (7): AFM image of S3 sample at 400 pulses

Figure (8): AFM image of S4 sample at 500 pulses

Table (2) shows the values of roughness and particle size measured by (AFM)

| Sample | Pulses number | Surface roughness (nm) | Average Grain Size (nm) |
|--------|---------------|------------------------|-------------------------|
| S1     | 200           | 7.78                   | 72.60                   |
| S2     | 300           | 4.06                   | 67.60                   |
| S3     | 400           | 3.73                   | 49.06                   |
| S4     | 500           | 2.82                   | 38.15                   |

3. Optical Properties Results

The UV–visible absorption spectra results, showed that the absorbance and absorption coefficient change as a function of the wavelength of the GO-Ag NPS thin film deposited on quartz slides. Shows as the absorbance increases with the increase in the number of pulses at wavelengths from (400 - 480 nm) for the silver element, and this came from the effect of the surface Plasmon resonance of Ag NPs, Which represents the collective excitation of the surface electrons of the outer shells as well as indicating a
decrease in the grain size, which led to blue shift [19]. A strong absorption peak at 230 nm, which is due to the $\pi - \pi^*$ transitions of aromatic C-C bonds. This corresponds and agreement with results of the (XRD, AFM). Also, we note as in Figure (9-10) the absorbance and absorption coefficient increased by increasing the number of pulses and this is due to the increase in the thickness of the thin film. The absorbance and absorption coefficient peaked at about (233 nm) wavelength for graphene oxide. While Figure (11) shows that transmittance decreases at wavelengths with high absorption and increases at wavelengths above 480 nm. As for the energy gap, Figure (13-a, b, c, d) and table (3) below show that it decreases with the increase in the number of pulses, due to the increase in the thickness of the thin film, and this is due to the increase in localized energy levels between the conduction and valence beams, which leads to an increase in absorption, and this results in agreement with Ratan et.al. [20]. The extinction coefficient have the same behavior with absorption coefficient that increase at higher wavelength up to (390 nm) and decrease after (400 nm) due to relaxation processes.

![Figure (9) The absorbance Spectrum with different pulses](image1)

![Figure (10) The absorption Coefficient Spectrum with different pulses](image2)

![Figure (12) The Extinction Coefficient with different pulses](image3)
Figure (11) The Transmittance Spectrum with different pulses

Figure (13-a) Plot of $(\alpha \hbar \nu)^2$ versus $\hbar \nu$ of S1

Figure (13-b) Plot of $(\alpha \hbar \nu)^2$ versus $\hbar \nu$ of S2

Figure (13-c) Plot of $(\alpha \hbar \nu)^2$ versus $\hbar \nu$ of S3

Figure (13-d) Plot of $(\alpha \hbar \nu)^2$ versus $\hbar \nu$ of S4
Table (3) shows the Energy gap

| Sample | Energy gap (eV) |
|--------|----------------|
| S1     | 3.38           |
| S2     | 3.25           |
| S3     | 3.12           |
| S4     | 2.9            |

4. Conclusions

The pulse laser deposition method can be used to form thin films with high efficiency, speed and low cost. The crystallite size decreases as the number of laser pulses increases with constant laser pulse energy. The surface roughness decreases and the grain size increases with the increase in the number of laser pulses with constant laser pulse energy. The absorption peak increases when the number of pulses increases due to the increase in the thin film thickness to the increase in the density of the metal nanoparticles in it, and this was shown by the results of the (UV) examination.

5. References

[1] A. Muheisin, “Study of Electrical Conductivity for Amorphous and semi crystalline polymers filled with Lithium Fluoride Additive”, M. Se. Thesis, College of Science, University of Mustansiriah, 2009.

[2] Das, I., and Ansari, S. A., " Nanomaterials in Science and technology", Scientific and industrial research, Vol. 68, 2009.

[3] Rao, C. N. R., Müller, A., and Cheetham, A. K., (Eds.), " The Chemistry of Nanomaterials: Synthesis, Properties and Applications". John Wiley and Sons, 2006.

[4] R.A. Smith, “Semiconductors”, 2nd Edition, (Cambridge University press), 1987.

[5] F.A. Shirland, “Solar Cells”, edited by Bachus C.E. IEEF press NewYork, p:36, 1976.

[6] L.E. Ckertov, “Physics of Thin Films”, Plenar Press, New York, 1977.

[7] S. Asaftei, E. De Clercq, "Viologen dendrimers as antiviral agents: the effect of charge number and distance", Journal of Medicinal Chemistry, 2010.

[8] Ben.G.Streetman, “Solid State Electronic Devices “, (Prentice-Hall of India. Private Limited New Delhi), 1991.

[9] M. R. Das, R. K. Sarma, R. Saikia, V. S. Kale, M. V. Shelke , P. Sengupta, Synthesis of silver nanoparticles in an aqueous suspension of graphene oxide sheets and its antimicrobial activity . Colloids and Surfaces B: Biointerfaces 8311622, 0927-7765. 2011.

[10] J. S and Fuge. M. G. Claeyssens. F. Ashfold. R. N. M] [Thin of Deposition and Ablation Laser Pulsed, “Henley Bristol of University, Chemistry of School”. Films. 2004.

[11] Chiu, L.A., Seraphin, A.A. and Kolenbrander, K.D., J. Electron. Mater. (1994).

[12] Al-Kinany, Maha, Ghaileb A. Al-Dahash, and Jasim Al-Shahban. "Effect of laser Fluence Energy on Morphological, Structural and Optical Properties of Gold and Silver Thin Films Prepared by Pulse Laser Deposition Method." Engineering and Technology Journal 33.9 Part (B) Scientific (2015).

[13] Maha Al-Kinany, Ghaileb A. Al-Dahash, Jasim Al-Shahban, Journal of Nanostructures (Growth, Characterization of Cu Nanoparticles Thin Film by Nd: YAG Laser Pulses Deposition). 2014.

[14] Ahmed Alaa Kandoh et al 2021 IOP Conf. Ser.: Earth Environ. Sci. 790 012073

[15] H.M. Smith and A.F. Turner,"Pulse Laser Deposition -Versatile Thin Film Technique", Appl. Optic., (1965).

[16] K. P. Loh, Q.L. Bao, P. K. Ang, J. X. Yang, The chemistry of graphene. Journal of Chemistry, 20 12 22772289, 0959-9428, 2010.
[17] Mónica Cobos, Iker De-La-Pinta, Guillermo Quindós, M. Jesús Fernández and M. Dolores Fernández "Graphene Oxide–Silver Nanoparticle Nano-hybrids: Synthesis, Characterization, and Antimicrobial Properties", Nanomaterials 2020, 10(2), 376.
[18] Torrisi, L., et al. "Gold nanoparticles produced by laser ablation in water and in graphene oxide suspension." Philosophical Magazine 98. 24 (2018): 2205-2220.
[19] Jwad Sahar, Y., & Shamran Mohammed, H. (2019). Synthesis and characterization some complexes of azo dye of pyrimidynyl and evaluating their biological activity. Al-Qadisiyah Journal Of Pure Science, 24(3).
[20] Ahmed Sabah Al-Jasimee et al 2020 J. Phys.: Conf. Ser. 1664 012141.
[21] A. Ghazay, A., Mayar Hezam, A., M. Alkhazaie, M., & Obayes, I. S. (2020). Study the effect of different temperatures on the biofilm production in Proteus mirabilis isolated from urinary tract infection patients. Al-Qadisiyah Journal Of Pure.
[22] Salah, A. (2020). The New Combination of Semi-Analytical Iterative Method and Elzaki Transform for Solving Some Korteweg-de Vries Equations. Al-Qadisiyah Journal Of Pure Science, 25(1), Math. 23 -26.
[23] Salam Hussein Ewaid et al 2021 IOP Conf. Ser.: Earth Environ. Sci. 722 012008
[24] Ali , W., & R.Anon, M. (2020). Biological Effective of organic solvent extracts of Mirabilis jalapa Leaves in the Non-cumulative for mortality of Immature stages Culex quinquefasciatus Say (Diptera : Culicidae ). Al-Qadisiyah Journal Of Pure Science, 25(1), Bio 1-6.
[25] Salam Hussein Ewaid et al 2020 J. Phys.: Conf. Ser. 1664 012143.
[26] Sami Abd ali , mohammed, Shaker Hussein, A., & mohammed hadi, H. (2020). Study The Current Density-Voltage (J-V) Characteristics of α-Fe2O3 Thin Film Prepared by Spray Pyrolysis Technique. Al-Qadisiyah Journal Of Pure Science, 25 (1), Phys 1-7.
[27] Al-Assaly, Rafal, Sadiq Hassan Lefta, and Amer Al-Nafiey. "Synthesize rGO-AG NPs by Pulse Laser Ablation in Less Pulse Energy and Ablation Time." (2020).
[28] Salam Hussein Ewaid et al 2021 IOP Conf. Ser.: Earth Environ. Sci. 790 012075
[29] M. M. Alvares, J. T. Khoury, T.G. Schaaff, M. N. Shafigullin, I. Vezmar, and R. L. Whetten, Optical absorption spectra of nanocrystal gold molecules, J. Phys. Chem. B 101 (1997). Pp 3706-3712.
[30] Ratan D., Siddarth S. Nath , Dipankar Chakdar, Gautam G. and Ramenddhu D." Synthesis of silver nanoparticles and their optical properties "Journal of Experimental Nanoscience, 2010.