Pulsed Laser Deposition to Investigate Structural and Optical Properties of Lead Sulfide Nanostructure

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Abstract
In this work, the structure and optical properties of Lead sulfide PbS nanostructure were studied. Thin film deposited on glass substrates were prepared by pulse laser deposition Nd:YAG laser at (1064 nm) wavelength with a various laser energies (200, 300, 400 and 500) mJ was used. The effect of changing the laser energy on the structural properties has been studied using atomic force microscope (AFM) and X-ray diffraction technique. It has been observed that the film formed is of the polycrystalline type and the predominant phase is the plane (111) and (200). AFM assays also showed that the minimum granular size obtained was (59.43 nm) at laser power (200 mJ). The results revealed the possibility of preparing nanostructure with medium grain size of (68 nm). As for the optical properties, the effect of changing the laser energy on nanostructure was studied, and it was found that they have direct allowed transitions in the range of (1.47 to 1.80) eV.

Key words
Nanostructure, nanoparticles, pulse laser deposition and lead sulfide.

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Introduction
The deposition method by pulsed laser ablation is one of the best and low coast techniques for the deposition of semiconductors, metals, and their oxides under different technological conditions [1]. Deposition by laser ablation technology was first used in the manufacture of nanostructure in the 1960s [2]. Pulsed laser deposition (PLD) preferably uses high-power laser pulses with an energy density of more than 108 (W/cm²L) which will precipitate a thin layer of a single target. This type (PbS) of semiconductor material is mostly prepared in the form of nanostructure [3, 4]. Lead sulphide (PbS) is an important direct narrow gap semiconductor material with an approximate energy gap of 0.4 eV at 300K and a relatively large excitation Bohr radius of 18nm [5]. In this category, PbS is a IV-VI compound semiconductor which has a cubic lattice with unit cell face center cubic. These properties make PbS very suitable for infrared detection applications.

However, it has wide and very important applications in the fields of manufacturing photovoltaic devices for example detectors and nanoscale solar cells because of its unique optical properties [6, 7]. It has a large absorption coefficient of about (10^5) cm⁻¹ in the visible range [8]. There are several techniques for nanostructure preparation, for example: including chemical deposition (CBD), thermal evaporation, spray deposition, and plasma atomization method. This research aims to manufacture nanostructures of PbS and to study the effect of changing the energy of the laser pulse on the structural and optical properties [9].

Experimental work
The pulse laser deposition (PLD) technique was used which is located in the plasma Research Laboratory in the Physics Department at the College of Science, University of Baghdad. The experiment was conducted in a vacuum chamber under vacuum conditions (2.5×10⁻² mbar). The PbS target was formed under 6-ton pressure for 10 minutes using a hydraulic type (SPECAC) piston to form a disc of target material with a (1.5 cm) and (0.3 cm) diameter and a thickness, respectively. In this work, glass slides have been used to study the structural and morphological properties of PbS nanostructure.

Nd:YAG laser of wavelength (λ), power (E) 200,300,400,500) mJ, frequency(f) 6Hz, and number of shots of 100 pulses. The incident Nd:YAG SHG Q-switching laser beam that comes through the window makes an angle of about 45 degrees with the target surface. The system consists of two vacuum systems, the first vacuum is called a rotating vacuum system with two stages, as well as, a pressure and temperature gauge and a vacuum chamber. The nanostructure was examined, the crystal structure and morphology were studied by X-ray diffraction (XRD) and atomic force microscopy (AFM). The nanostructure was also examined by ultraviolet spectroscopy (UV) to determine the optical properties.

Results and discussion
Structural properties
X-ray diffraction
Fig.1 shows the results of the X-ray diffraction examination, which shows three main peaks of lead sulfide representing the crystal planes of the cubic crystal structure (111), (200) and (220) corresponding to the angles (25.8196°, 29.9899° and 43.0319°) respectively, according to the card (96-901-3404). It is also noticed that there are two main peaks of lead, representing crystalline planes (111) and (200) corresponding to the angles (31.11° and 36.1°) respectively, and according to the numbered card (96-
901-2960). It shows a high degree of crystallinity, the crystal size changed from (10.5 nm to 26 nm) by increasing the laser power.

![XRD spectra](image)

**Fig.1: The X-RD spectra of PLD-prepared lead sulfide nanostructure with different laser energies.**

The crystal size was calculated using Eq. (1) (Table 1). The crystallitesize (D) of a crystalline material can be easily estimated from the X-ray spectrum by means of the full width at half-maximum peak (FWHM). It can be calculated by the Scherrer’s formula [10]:

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

(1)
where \( \lambda \) represents the X-ray wavelength=(0.15406) nm, \( \Theta \) represents Bragg’s angle, and \( \beta \) represents the full width at half-maximum peak (FWHM) in units of radial angles.

In addition, the dislocation density (\( \delta \)) of PbS nanostructures were determined using the following relations:

\[
\delta = \frac{1}{D^2}
\]  

(2)

Table 1: Effect of laser energy on the structural properties of PbS nanostructure.

| E (mJ) | 2\( \Theta \) (Deg.) | FWHM (Deg.) | \( d_{\text{hkl}} \) Exp. (\( \text{Å} \)) | C.S PbS | Av. C.S PbS (\( \times 10^3 \) lines/m\(^2 \)) | (\( \delta \))\( \times 10^3 \) (lines/m\(^2 \)) | \( d_{\text{hkl}} \) Std. (\( \text{Å} \)) | Phase | hkl |
|------|----------------|-------------|----------------|--------|----------------|----------------|----------------|------|-----|
| 200  | 25.8196        | 0.9000      | 3.4478         | 9.1    | 7.23           | 3.4246         | Cub.PbS        | (111) |
|      | 29.9899        | 0.7333      | 2.9772         | 11.2   | 4.97           | 2.9657         | Cub.PbS        | (200) |
|      | 31.1170        | 0.6300      | 2.8719         | 13.1   | 3.2            | 2.8519         | Cub.Pb         | (111) |
|      | 36.1069        | 0.1800      | 2.4856         | 46.4   | 1.55           | 2.4698         | Cub.Pb         | (200) |
|      | 43.0319        | 0.7600      | 2.1003         | 11.2   | 2.65           | 2.0971         | Cub.PbS        | (220) |
| 300  | 25.8495        | 0.9400      | 3.4439         | 7.8    | 16.28          | 3.4246         | Cub.PbS        | (111) |
|      | 30.0033        | 0.6400      | 2.9759         | 12.9   | 6.05           | 2.9657         | Cub.PbS        | (200) |
|      | 31.1944        | 0.6650      | 2.8649         | 12.4   | 6.5            | 2.8519         | Cub.Pb         | (111) |
|      | 36.3067        | 0.4200      | 2.4724         | 19.9   | 2.52           | 2.4698         | Cub.Pb         | (200) |
|      | 43.1418        | 0.5400      | 2.0952         | 15.8   | 3.99           | 2.0971         | Cub.PbS        | (220) |
| 400  | 25.9294        | 0.6934      | 3.4335         | 11.8   | 12.19          | 3.4246         | Cub.PbS        | (111) |
|      | 30.0433        | 0.5800      | 2.9720         | 14.2   | 7.94           | 2.9657         | Cub.PbS        | (200) |
|      | 31.2019        | 0.4666      | 2.8643         | 17.7   | 5.83           | 2.8519         | Cub.Pb         | (111) |
|      | 36.1119        | 0.3300      | 2.4853         | 25.3   | 0.46           | 2.4698         | Cub.Pb         | (200) |
|      | 42.9519        | 0.4400      | 2.1040         | 19.4   | 7.92           | 2.0971         | Cub.PbS        | (220) |
| 500  | 25.8860        | 0.3533      | 3.4391         | 23.1   | 1.87           | 3.4246         | Cub.PbS        | (111) |
|      | 29.9933        | 0.3000      | 2.9769         | 27.4   | 1.33           | 2.9657         | Cub.PbS        | (200) |
|      | 31.2058        | 0.2480      | 2.8639         | 33.3   | 0.9            | 2.8519         | Cub.Pb         | (111) |
|      | 36.2368        | 0.2000      | 2.4770         | 41.8   | 0.57           | 2.4698         | Cub.Pb         | (200) |
|      | 43.0069        | 0.3100      | 2.1014         | 27.5   | 1.31           | 2.0971         | Cub.PbS        | (220) |

**Atomic Force Microscope (AFM) analysis**

Figs. 2(a, b, c, d) show images of atomic force microscope (AFM) with different pulse laser energies (200, 300, 400 and 500 mJ). Where the presence of a smooth surface and high-quality adhesion to the glass base was found, in addition to the formation of semi-spherical clusters with close grain sizes. The surface of the nanostructure is the result of an increase in the proportion of scraping that leads to an increase in the granular size, when increasing the laser energy from 200 to 500 and this is evident in Table 2 i.e. The number of particles is few within this area. What happens during the deposition process is that the layers of the nanostructure, through the interaction of the ablation products inside the plasma such as ions and the uncharged ablation fractions with different diffusion speeds, reach the surface of the nanostructure. The fragments of high energies (fast) represent the ions, while the velocity of the uncharged fragments is determined by the multiplicity of collisions.
with the charged particles. Accordingly, the skimming or excision with high laser energy leads to an increase in the possibility of the emergence of large granules after many collisions, which leads to an increase in the roughness of the nanostructure surface. This was observed in the results of the atomic force microscopy. This agrees with the results of Al-Kinany et al. [11].

**Fig.(a):** AFM images for nanostructure at energy 200 mJ with (Avg. Diameter 59.34 nm).

**Fig.(b):** AFM images for nanostructure at energy 300 mJ with (Avg. Diameter: 60 nm).

**Fig.(c):** AFM images for nanostructure at energy 400 mJ with (Avg. Diameter: 74.49 nm).

**Fig.(d):** AFM images for nanostructure at energy 500 mJ with (Avg. Diameter: 80 nm).

**Fig.2:** Topographical images of PbS nanostructure at different laser energies.
Table 2: The AFM analyze parameters of PbS nanostructure with different laser energies at a constant thickness (t~200 nm).

| Sample | Energy (mJ) | Grain size (nm) | Ave. Roughness (nm) | Peak-peak (nm) | Root Mean Sq. (nm) |
|--------|-------------|----------------|---------------------|----------------|-------------------|
| PbS    | 200         | 59.34          | 2.53                | 9.88           | 2.91              |
|        | 300         | 60             | 4.37                | 21.1           | 5.16              |
|        | 400         | 74.49          | 5.54                | 28.2           | 6.56              |
|        | 500         | 80             | 8.5                 | 35             | 9.85              |

Optical properties

In this work, the effect of laser energy on the optical properties of PbS nanostructure that were deposited at room temperature on glass substrates were studied using UV-Vis spectroscopy.

The Absorbance Spectrum (A)

Through the absorption spectra shown in Fig.3, it was found that the absorbance increases with the increase in the energy of the laser pulse.

![Fig.3: Absorbance of PbS nanostructure deposited at different laser energies as a function of wavelength.](image)

The maximum absorbance peak at (500 mJ) is located in the UV region because the main absorption edge of the material (PbS) is located in this region. Increasing the wavelength, the absorbance begins to decrease down to the visible region. This behavior shows that at short wavelengths an interaction would occur between the incident photon and the material, and thus the photon would be absorbed by the material, and this results in transitions between the vibration levels of nanoparticles within the inner bundles of the material particles. But, as the wavelength is increased, the photon does not have sufficient energy to interact with the atoms of the material. Therefore, it will be scattered. It was noticed that the increase in energy leads to an increase in surface roughness, and so absorption will increase.

The Transmission Spectrum (T)

The transmittance spectrum changes as a function of the PbS nanostructure wavelength. After using the equation [11]:

\[ A = \log \left( \frac{1}{T} \right) \]  

(3)
The transmittance spectra can be plotted as shown in Fig. 4. It was found that transmittance decreases with the increase in the energy of the laser pulse. This is due to the increase in the skimming percentage, which leads to an increase in the average grain size. The maximum transmittance rate at energy (200 mJ) was noticed to lie in the IR region at the wavelength ($\lambda_{\text{max}} > 1000$ nm), where the transmittance ratio is (76.5). It was observed that all PbS nanostructure prepared with PLD technology have the highest value of optical transmittance at high wavelengths. This agrees with the results of Al-Kinany [12].

![Transmittance spectra](image)

**Fig. 4: Transmittance of PbS nanostructure deposited at different laser energies as a function of wavelength.**

**Absorption coefficient ($\alpha$)**

The absorption coefficient ($\alpha$) was calculated according to the equation [13]:

$$\alpha = \frac{(2.303 \times A)}{t}$$

($\alpha$ of the PbS nanostructure was found to change as a function of wavelength. This is shown in Fig. 5. It was observed that the absorption coefficient ($\alpha$) of PbS films increased from $9 \times 10^4$ cm$^{-1}$ to $42 \times 10^4$ cm$^{-1}$. It reached its greatest magnitude at the wavelength ($\lambda_{\text{max}} = 400$ nm). The increase in the grain size as a result of the increase in the energy of the laser pulse led to an increase in the absorption. As the greatest absorption of the photon is located in the ultraviolet region, therefore the greatest energy of the photon, is located in this region because it contains a short range of wavelengths. ($\alpha > 10^4$ cm$^{-1}$) the type of transition is of the direct transition, and this is consistent with the results of Eya [15].

![Absorption coefficient](image)

**Fig. 5: Absorption coefficient of PbS nanostructure deposited at different laser energies as a function of wavelength**
Reflectance

The reflectivity (R) was obtained using the equation [14]:

\[ R = 1 - T - A \]  \hspace{1cm} (5)

Fig.6 shows the change of reflectivity as a function of wavelength.

Fig.6: Reflectivity R of PbS nanostructure deposited at different laser energies as a function of wavelength.

Optical Energy Gap (Eg)

The optical energy gap is one of the most important optical constants in semiconductor physics. The use of semiconductors in optical and electronic applications depends on the value of this constant (Eg) [15]. The energy gap value depends on the crystal structure of the material. Its value (Eg) can be determined by knowing the value of the absorption coefficient and the energy of the incident photon. Using the equation [16]:

\[ (\alpha h\nu) = A(h\nu - E_g)^r \]  \hspace{1cm} (6)

And through Fig.7, the energy gap was calculated for the PbS films deposited on glass slides at variable energies of (200 mJ - 500 mJ). It was found that its value ranges between (1.47-1.8) eV (Table 3). A decrease in the energy gap values was observed with the increase in the energy of the laser pulse. This decrease of (Eg) indicates an increase in the particle size of the material due to the irritation of the secondary levels within the energy gap, as a result the width of the energy gap decreases and the largest number of granules on the surface of the slide was noticed. This is in agreement with the results of T. A. Faiadh [13].

Fig.7: \((\alpha h\nu)^2\) of the prepared PbS nanostructure as a function of the photon energy at different laser energies.
Refractive index (n)

Fig. 8 shows the change of the refractive index of PbS nanostructure deposited on glass slides as a function of wavelength. The refractive index was calculated using equation [17]:

\[ n = \left[ \left( \frac{1+R}{1-R} \right)^2 - (k^2 + 1) \right]^{1/2} + \frac{1+R}{1-R} \]  

(7)

where R: Reflection and k: Extinction Coefficient. It was noticed from the figure that with the increase in the energy of the laser pulse, the refractive index decreased and increased gradually with an increase in the wavelength. The nanostructure present with energy of 200mJ has the highest refractive index at wavelength (1064) nm, and this corresponds to the researcher's results [18].

![Fig. 8: Refractive index (n) of PbS nanostructure deposited at different laser energies as a function of the wavelength.](image)

Extinction coefficient (k)

The extinction coefficient (k) represents the amount of energy absorbed in the nanostructure, and more precisely, it represents the inactivity of the electromagnetic wave inside the material.

Fig. 9 shows the change of the coefficient of extinction coefficient of the PbS membranes as a function of wavelength, that was calculated using the equations [19]:

\[ K_o = \alpha \lambda / 4\pi \]  

(8)

![Fig. 9: Extinction coefficient (k) of PbS nanostructure deposited at different laser energies as a function of wavelength.](image)
It was observed that the extinction coefficient increased with the increase in the energy of the laser pulse and that the nanostructure with laser energy (500 mJ) recorded the highest extinction coefficient. This result agrees well with the results of AADIM et al. Abbas [8].

**Dielectric constant**

The dielectric constant is another important visual parameter that can be calculated. Figs. 10 and 11 show the difference in real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of dielectric constant values for PbS nanostructure as a function of wavelength in the range 300 to 1100 nm. Real and imaginary dielectric constants were calculated using the given equations [20, 21]:

$$\varepsilon_r = n^2 - k^2 \quad (9)$$

$$\varepsilon_i = 2nk \quad (10)$$

The behavior of ($\varepsilon_r$) is similar to that of the refractive index. Due to the smaller value of $k^2$ compared to $n^2$, it was found that ($\varepsilon_r$) decreases with increasing the energy of the laser pulse. This is due to the decrease in the refractive index values and the increase in the extinction coefficient values with increasing the laser pulse energy. As for the imaginary part of dielectric constant ($\varepsilon_i$), its value increased with the increase in the energy of the laser pulse, for it mainly depends on the values of the extinction coefficient $k$, as shown in Table 3. Fig. 11 shows ($\varepsilon_i$) for PbS nanostructure as a function of the wavelength in the range 400 to 1100 nm.

**Fig.10:** The variation of the dielectric constant real part ($\varepsilon_r$) of PbS nanostructure with wavelength for different laser energies.

**Fig.11:** The variation of the dielectric constant imaginary ($\varepsilon_i$) part of PbS nanostructure with wavelength for different laser energies.
Table 3: The optical parameters of PbS nanostructures for different laser energies at wavelength $\lambda = 500$ nm and thickness $t=200$ nm.

| E (mJ) | T%   | $\alpha$ (cm$^{-1}$) | K   | n   | $\varepsilon_r$ | $\varepsilon_i$ | Eg (eV) |
|--------|------|----------------------|-----|-----|-----------------|-----------------|---------|
| 200    | 53.06| 91899                | 0.366| 2.676| 6.702           | 1.885           | 1.80    |
| 300    | 42.36| 120263               | 0.479| 2.643| 6.557           | 2.531           | 1.72    |
| 400    | 29.20| 166193               | 0.662| 2.428| 5.455           | 3.212           | 1.60    |
| 500    | 24.27| 205312               | 0.817| 2.213| 4.228           | 3.617           | 1.47    |

Conclusions

Through the results of the X-ray diffraction examination, it was clear that the PbS polycrystalline nanostructure has a cubic structure. It also showed that the rate of crystal size increases with the increase of the laser power. In addition, according to the results of the atomic force microscope (AFM) scan, it was noticed that the higher the laser power, the higher the grain size. Also, from the study of the optical properties of the PbS nanostructure, it was found that the energy gap decreases as the energy of the laser increases.

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