

# Depositing Layers of Nano Graphene on P-Type Silicon Substrate and Studying the Structural and Optical Properties

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## ABSTRACT

The present study involved the deposition of graphene films onto a silicon substrate of p-type using the Pulsed Laser Deposition (PLD) technique by varying the number of laser pulses (700, 600, and 500 pulses) at a fixed energy of 800 mj and a frequency of 6 Hz. The thickness of the prepared samples was calculated, revealing a significant increase in thickness (from 282 to 223 nm) attributed to the accumulation of material with increasing number of pulses. X-ray diffraction (XRD) patterns of graphene samples showed an increase in both the degree of crystallinity and the intensity of the graphene peak with increasing number of pulses leading to an initial boost in crystalline growth. The utilization of (SEM) images, particularly in samples created with 700 pulses, they appear to be more extended and smoother, forming wavy surfaces. Furthermore, a discernible augmentation in the quantity of graphene atomic layers was seen from 80 to 116 in samples that underwent an increase in the number of pulses from 500 to 700. The observation revealed a distinct arrangement of the surface, where, these layers effectively covered the surface with a thickness measuring 115 nm. Furthermore, a noticeable variation in the surface morphology of the deposited samples was also observed with increasing number of pulses. FTIR spectra exhibited a conspicuous augmentation in the intensity of bands, particularly for the asymmetric and symmetric vibrations of the CH<sub>2</sub> group, which manifest at wavenumbers of 2940 and 2890 cm<sup>-1</sup>, respectively, concomitant with an escalation in the number of laser pulses employed during the deposition procedure.

**Keywords-** p-type silicon, Pulsed Laser Deposition (PLD) technique, nanoscale graphene.

## I. INTRODUCTION

The phrase "thin films" is employed to denote a singular or multiple layers of a certain substance, characterized by a thickness that falls between the range of 10 nanometers to less than one micrometer, hence rendering them exceedingly thin. The deposition of thin film layers is carried out on carefully selected substrates or bases, taking into consideration the specific requirements of the study or scientific objectives. These substrates may include glass slides, silicon wafers, aluminum, quartz, and various other materials. The physical characteristics of thin films exhibit variations in comparison to those associated with bulk materials [1]. The production of thin films was initially accomplished by Busen and Grove in 1852 through the utilization of chemical reactions. In the year 1857, Faraday achieved the successful production of a thin metallic film by means

of thermal evaporation. Thin films have been utilized in several applications, including the production of p-n junction transistors, rectifiers, integrated circuits, optical communications, light-emitting diodes, semiconductor lasers, detectors, and solar cells [2].

Nanomaterials are characterized as materials whose dimensions in at least one direction or internal grain size fall within the range of 1 to 100 nanometers (nm). The reduced dimensions of these materials have resulted in distinct behavior that deviates dramatically from standard materials of greater sizes, surpassing 100 nm. These materials have distinctive qualities and traits that are absent in conventional materials. Nanomaterials are widely recognized as the fundamental constituents of contemporary technological advancements in several fields such as nanotechnology, information and communication technology, and biotechnology. Gross Domestic Product (GDP) serves as a metric for assessing

a nation's development and serves as an indicator of its progress.

Nanomaterials exhibit a diverse range of origins, covering both organic and inorganic materials, as well as natural and manmade compounds. Various technical materials, including metallic elements, their alloys, semiconductors, oxides, and metals, have the ability to exist in nano-scale forms. These nano-forms can be obtained from both natural and synthetic sources [3].

Nanocrystalline graphene refers to a slender structure consisting of carbon atoms that are intricately linked together, forming a sheet with a thickness equivalent to that of a single carbon atom. The atoms exhibit intermolecular bonding, forming hexagonal patterns that bear resemblance to the characteristic structure of honeycomb cells. The distinctive architecture of this structure confers remarkable mechanical properties, like as strength and hardness, to graphene, while still preserving its thinness and large surface area. Graphene is widely acknowledged as the most robust substance currently known on Earth, surpassing the strength of diamond by a factor of four and steel by a factor of 300 [4]. Furthermore, graphene possesses exceptional thermal and electrical conductivity attributes as a result of its two-dimensional structure.

The primary objective of the present study is to fabricate thin films composed of nanocrystalline graphene that are deposited onto p-type silicon substrates through the utilization of Pulsed Laser Deposition (PLD) technology. The desired material is fabricated into disk-shaped pellets utilizing powder metallurgical methodologies. The research is centered around the

examination of the structural, optical, and morphological characteristics of the films that were created.

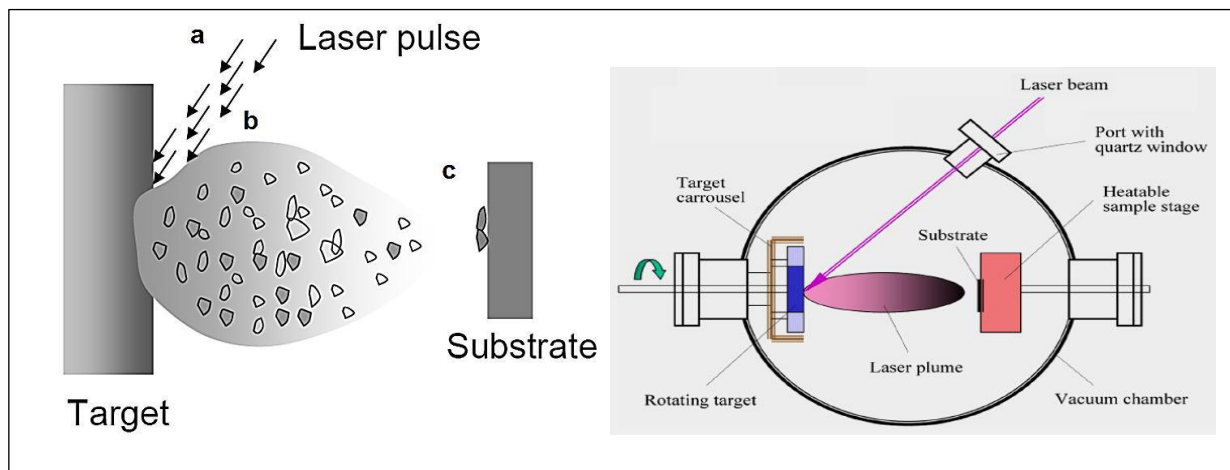
## II. MATERIALS & METHODS

### 1. Pulsed Laser Deposition (PLD)

The Pulsed Laser Deposition (PLD) technique comprises three main steps: material ablation, high-energy beam formation, and film growth on a substrate using a high-energy laser. In this technique, a high-energy laser is used as an energy source to vaporize a target material containing the desired film components. When the laser beams are absorbed by a solid surface, the electromagnetic energy is converted into electronic excitation, as well as chemical, mechanical, and thermal energy, causing evaporation and plasma formation. (PLD) is a thin-film deposition method that utilizes short and intense laser pulses to evaporate the target material, which is then deposited onto a substrate as shown in Fig (1). The deposition process occurs in a vacuum chamber to minimize particle scattering. However, in some cases, reactive gases may be used to modify the stoichiometry of the deposits. The removal or ablation of the target material by laser targeting relies on coupling the laser beam with the solid material. The typical values for laser fluence used in PLD range from 1-10 J/cm<sup>2</sup> with pulse durations of 5-50 nanoseconds, depending on the material selection. These values are usually higher than the threshold value for plasma formation for most materials. A Nd:YAG pulsed laser device was operated according to the specified operational parameters mentioned in Table (1).

**Table (1): Operational Specifications of the Laser Device.**

Laser Mode	(Nd : YAG) Laser
Laser Wavelength	<b>1064 nm</b>
The used frequency.	<b>Hz(6)</b>
The energy used.	<b>(mj 1000- mj 900- mj 800)</b>
The number of pulses used.	<b>(puls700- puls600- puls500)</b>



**Figure (1): Schematic representation of the Pulsed Laser Deposition (PLD) deposition system.**

## 2. The materials used Graphene:

A monolayer of carbon atoms, has garnered considerable attention in the scientific community owing to its distinctive structure and extraordinary characteristics. Graphene is a planar substance consisting of carbon atoms that are purely bonded by SP<sup>2</sup> hybridization, exhibiting a regular hexagonal lattice structure reminiscent of the cells seen in beehives. This substance functions as the fundamental unit for the formation of graphite material and is widely recognized as one of the carbon nanomaterials. Graphene is composed of a 2D crystal lattice formed by interconnected carbon atoms. Within each unit cell, there are two atoms, denoted as B and A, which are positioned at a distance of approximately 1.42 angstroms ( $a_{c-c} = 1.42 \text{ \AA}$ ) from each other. The lattice vectors in three-dimensional space are conventionally characterized as a set of three linearly independent vectors that span the lattice. These vectors determine the periodicity and symmetry of the lattice structure.

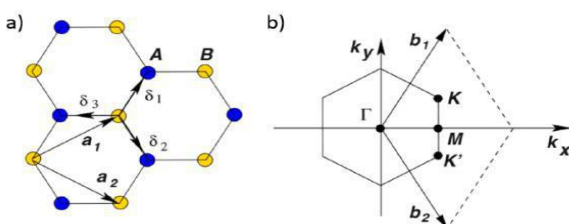
$$\mathbf{a}^{\rightarrow}_2 = \frac{\mathbf{a}_{c-c}}{2} (3, -\sqrt{3}) / \mathbf{a}^{\rightarrow}_1 = \frac{\mathbf{a}_{c-c}}{2} (3, \sqrt{3})$$

The lattice constants in space are:  $\|\mathbf{a}^{\rightarrow}_1\| = \|\mathbf{a}^{\rightarrow}_2\| = a = 2.456 \text{ \AA}$

We have the unit vectors  $\hat{K}$  and  $\hat{K}'$

$$\hat{K} = \left( \frac{2\pi}{3a_{c-c}}, -\frac{2\pi}{3\sqrt{3}a_{c-c}} \right) \text{ and } \hat{K}' = \left( \frac{2\pi}{3a_{c-c}}, \frac{2\pi}{3\sqrt{3}a_{c-c}} \right)$$

The graphene used is in powder form, and its morphological shape consists of black-colored platelets. The thickness of these platelets is approximately 6-8 nanometers, while the lateral dimension (diameter) is approximately 15 micrometers.



**Figure (2): Dimensions of the graphene unit cell [13]. Stearic acid (C18H36O2) is the binding material used.**

The substance is white granules with the chemical formula C18H36O2 and a molecular weight of 284.48. It is of Indian origin and is used as a binding material for graphene.

### Silicon (Si) substrates

The substrate for the samples consisted of p-type silicon. The crystal orientation that exhibited dominance was (111), while the resistance values spanned from (1-10 ohms). The objects were divided into rectangular shapes with diameters measuring (1-2 cm).

## III. SAMPLE PREPARATION AND PROCEDURES

### Deposition Substrate Preparation

The preparation of the substrates for thin film deposition involves several stages. The substrates were first cut into rectangular shapes with dimensions of (1 × 2). They were then immersed in a container containing 96% pure ethanol to remove any potential contaminants. Afterward, they were left to air-dry for a few minutes.

### Preparation of weight ratios

Preparing a mixture by weight ratio of (2 gm) of graphene with the addition of (0.005 gm) of the binding material stearic acid on a high-sensitivity digital balance with a precision of (10<sup>-4</sup> gm). The ratios were manually mixed for 15 minutes to achieve the highest level of material mixing and preparation for compression. The materials were compressed under high pressure in stainless steel molds for graphene and the mixed binding material at a pressure rate of 5 bar for 15 minutes to form solid discs due to the high pressure, to be prepared as a target to be irradiated with pulsed laser.

## IV. RESULTS AND DISCUSSION

### 4-1 Structural Properties

Figure 3 shows X-ray diffraction patterns of graphene samples deposited using pulsed laser at a constant energy of 800 mJ and different numbers of pulses (500, 600, 700) on a silicon substrate of the p-type. All samples exhibit a high-intensity peak at diffraction angle of 29°, which corresponds to the silicon substrate with a single-crystal direction (111). Additionally, there is a peak located at around 26.2°, which matches the diffraction peak for the (002) crystallographic direction of graphene according to the (Joint Committee on Powder Diffraction Standards) JCPDS card (96-120-0018). The preferred growth direction of graphene is the (002) direction, which represents the direction perpendicular to the graphene layer. This direction corresponds to the c-axis in the hexagonal lattice structure.

The full width at half maximum (FWHM) of the graphene peak was determined using the X-powder program, as shown in the figure included within the figure. An increase in the number of pulses led to an increase in the degree of crystallization, evident from the increase in the intensity of the graphene peak, especially for samples deposited on p-type silicon. which promotes nucleation at the early stage of crystalline growth. Additionally, there is a decrease in the peak's exposure with an increase in the number of pulses, indicating an increase in the crystalline volume [15].

A slight shift in the peak can be observed from one sample to another due to the variation in lattice strain caused by the presence or absence of crystalline volume. The lattice strains were calculated using [X-powder] program. Furthermore, the dhkl interplanar distances were calculated using the Bragg's law equation based on

the  $2\theta$  diffraction angle. The crystalline volume was also calculated based on the peak broadening ( $\beta$ ) using the Debye-Scherrer equation. Since the  $d_{hkl}$  distances are equal within the same direction and represent the thickness of the graphene layer in the (002) direction, the number of atomic layers can be calculated by dividing the crystalline volume for this direction by the interplanar distances, as shown in Table (2) for samples deposited at different numbers of pulses on p-type silicon.

From the table, it can be observed that the crystalline volume in the (002) direction, which represents the thickness of the graphene layer, falls within

the nanoscale range for all samples, and it increases with an increase in the number of pulses used in deposition. There is also a noticeable increase in the number of carbon atomic layers from 80 to 116 for samples deposited on p-type silicon as the number of pulses increases from 500 to 700 pulses. On the other hand, lattice strains decrease with an increase in the number of pulses due to their inverse relationship with crystalline volume. This change in structural properties has a significant impact on the remaining physical properties, indicating that these properties can be controlled by adjusting the number of pulses used in deposition.

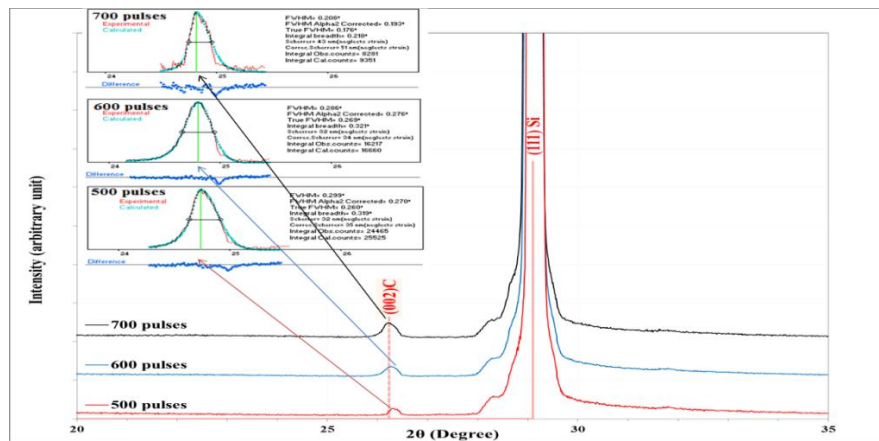


Figure (3): X-ray diffraction patterns for graphene samples deposited with different numbers of pulses at 800 mJ energy on p-type silicon substrates.

Table (2): X-ray diffraction parameters for graphene samples deposited with different numbers of pulses at 800 mJ energy on p-type silicon substrates.

Pulses	2θ (Deg.)	FWHM (Deg.)	$\beta$ (rad)	$d_{hkl}$ Exp.(Å)	D (nm)	No. of layers	Strain	hkl
500	26.2201	0.299	0.005	3.3961	27.3	80	0.00030	(002)
600	26.2250	0.286	0.005	3.3954	28.5	84	0.00029	(002)
700	26.3096	0.208	0.004	3.3847	39.2	116	0.00021	(002)

#### 4-2 Studying Nanoscale Topography of Sample Surfaces

Figure (4) shows scanning electron microscope (SEM) images of the graphene samples deposited with different numbers of pulses at an energy of 800 mJ on p-type silicon substrates. At 500 pulses, the samples appear as closely packed wrinkled flakes with thicknesses ranging from 100-160 nm. Increasing the number of pulses to 600 shows a mixture of granular particles along with the wrinkled flakes, with a thickness of about 35 nm. With 700 pulses, there is a clear formation of smooth and complete graphene layers evenly distributed on the surface, covering it with a thickness of 115 nm. There is a noticeable difference in the surface morphology of the samples deposited on the substrates, especially in the samples prepared using 700 pulses, where they appear to be more extended and smoother, forming wavy surfaces, as shown in Figure (8).

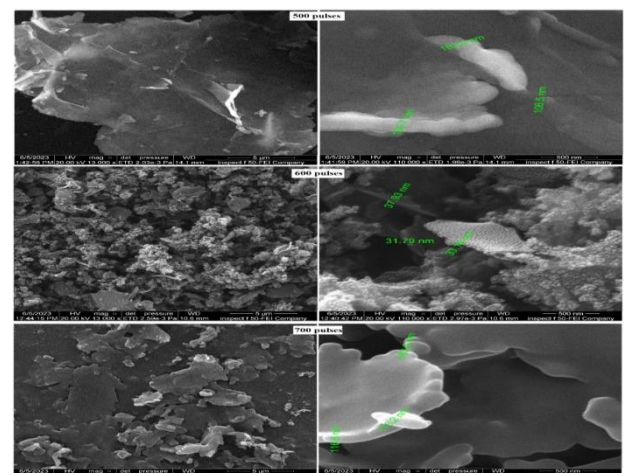


Figure (4): Scanning Electron Microscope (SEM) images of graphene samples deposited with different numbers of pulses at an energy of 800 mJ on p-type silicon substrates.

The difference in the structure or surface morphology of the deposited material with varying laser energy is a result of multiple effects in the deposition process and the material's interaction with the laser. Increasing the laser energy leads to more chemically active reactions between the material and the laser, affecting the material's structure and surface formation. The laser energy contributes to the evaporation and particle exchange from the sample's surface. This can lead to the formation of different structures based on the interactions and exchanges between atoms and molecules. Local heating can influence the deposition, fusion, and surrounding chemical reactions, contributing to changes in the structure and increased crystallization of the deposited material.

**4-3 Study of Bonds Using Fourier-Transform Infrared Spectroscopy (FTIR)**

Figure (5) shows Fourier-transform infrared spectra (FTIR) within the wavenumber range of 400 to 4000  $\text{cm}^{-1}$  for samples of graphene films deposited using different numbers of pulses on p-type silicon. All samples exhibit multiple regions related to molecular vibrations involving carbon bonding with other elements from the surrounding air, such as oxygen and hydrogen. Additionally, vibrations at 1613, 1544, and 1468  $\text{cm}^{-1}$  are related to the aromatic ring vibrations of graphene [16], as shown in Table (3). There is a clear increase in the intensity of bands, especially for the non-symmetric and symmetric CH<sub>2</sub> vibrations located at 2940 and 2890  $\text{cm}^{-1}$  [17], with an increase in the number of pulses used in deposition.

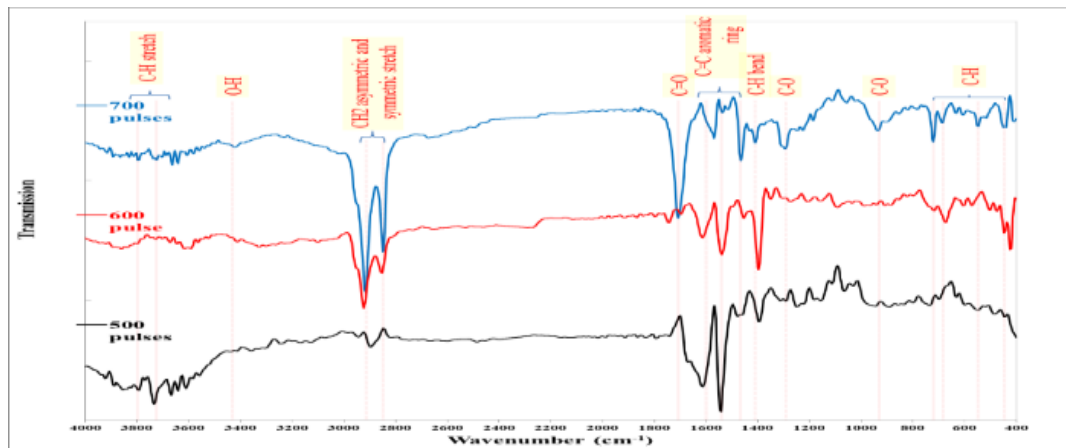


Figure (5): FTIR spectra for samples of graphene films deposited using different numbers of pulses on p-type silicon at an energy of 800 mJ.

Table (3): Vibrational band positions for FTIR spectra of graphene samples deposited with different numbers of pulses at an energy of 800 mJ.

Band Type	500 pulses	600 pulses	700 pulses
C-H stretch	-	3862.07	3797.70
	3735.63	3616.09	3724.14
O-H	-	-	3429.89
Asymmetric CH <sub>2</sub>	2944.83	2921.84	2914.94
Symmetric CH <sub>2</sub>	2896.55	2852.87	2848.28
C=O	-	1698.85	1705.75
Aromatic C=C	1613.79	1611.49	-
	1544.83	1542.53	1567.82
	1468.97	1455.17	1466.67
C-H bend	1388.51	1395.40	1409.20
C-O	1303.45	1344.83	-
	-	1275.86	1291.95
	1239.08	-	1225.29
	1154.02	-	-
	1068.97	1087.36	-
C-H	944.83	-	931.03
	891.95	891.95	721.84
	737.93	668.97	685.06
	549.43	572.41	549.43
	487.36	420.69	445.98

This increase in the intensity of the vibrations corresponding to the carbon-hydrogen groups is attributed to more efficient interactions between graphene and hydrogen in the surrounding atmosphere, leading to an improvement in the formation of chemical bonds and their impact on molecular regions. Furthermore, the increase in laser energy contributes to enhancing the effectiveness of the deposition process, thereby enhancing the observed vibrations in the FTIR spectrum. These observations highlight the increasing importance of the number of pulses as a variable in studying the effects of laser irradiation on the composition and chemical and molecular properties of samples.

## V. CONCLUSIONS

This research focused on preparing graphene films on silicon substrates using (PLD) under varying deposition conditions by altering the number of laser pulses. The chosen silicon substrate was of the p-type. The X-ray diffraction results showed two peaks, one at a diffraction angle of  $26^\circ$ , along with the distinctive silicon peak, indicating the formation of graphene layers. Increasing the number of laser pulses resulted in a noticeable improvement in film crystallinity and an increase in crystal size, extending beyond the nanoscale. This improvement in crystallinity was reflected in reduced lattice strains. The study demonstrated the ability to control the number of graphene layers by varying the number of laser pulses. Nanostructured formations in the form of twisted and stacked layers were observed, with thickness increasing significantly as the number of pulses increased, surpassing the nanoscale range and resembling rock-like structures. FTIR spectra revealed vibrational modes related to aromatic ring vibrations as well as vibrations associated with carbon-hydrogen and carbon-oxygen bonds. There were significant changes in peak intensities and shifts in their positions with an increase in the number of laser pulses. These thin films can be used in sensors, solar cells, and optoelectronic devices.

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