Characteristics Study of Silicon Nanoparticles Produced by Laser Ablation

A thesis submitted to the Department of Applied Sciences of University of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Laser Physics and optoelectronics

by

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وهي جزء من متطلبات نيل شهادة فلسفة دكتوراه في

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بباشراف

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4.1 Conclusions and Perspectives

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References
Pulsed Laser Ablation (Technique) for synthesizing the nano-sized silicon using a laser with a wavelength of 532 nm and a pulse energy of 1000 mJ and a pulse duration of 10 ns. The frequency is 1 Hz. The resulting material was subjected to a constant rate of 2.2 x 10^-4 torr.

To carry out an analysis of the transmittance and reflectance of the laser, the laser beam was directed to the target surface with a frequency of 28 Hz. The analysis was performed using the Cauchy's equations. The bandgap energy of the material was determined to be 2.8-2.5 eV.

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التحليل السطحي باستعمال مجهر القوة الذري (AFM) أظهر بان التركيب السطحي للاغشية المرسبة نانوي وبين بان تغيير طاقة الليزر من 300 - 500 mJ يزيد من خشونة السطح تغيير من 8.9 nm وعند طاقة ليزر (100 mJ) أصبح معدل الخشونة (٠٠٦ nm).

أضافة إلى ذلك تم استخدام المجهر الإلكتروني الماسح (SEM) لدراسة طبوغرافية السطح الصور اظهرت خليط من النقائق النانوية والقطرات بسبب عملية التبخير والذوبان حيث تبين بان الليزر الذي طول موجته (1064 nm) يودي الى اغشية سطحية اخفض وافضل مواصفات طبوغرافية. في نفس الوقت، الاغشية حضرت عند ليزر طوله الموجي (532 nm) يمتلك سطح انعم وقريب جدا من التركيب العشائي بسبب ان الطول الموجي (٠٤٢ nm) ي خترق بعمق الى الهدف يودي الى ارتفاع كبير في درجة الحرارة وحجم كبير من دقائق للمادة.
Pulsed laser ablation (PLA) technique of Si nanoparticles on glass with near-infrared (1064 nm), and visible (532 nm) emissions of a pulsed Nd:YAG laser were studied. Laser energy from 100 to 1000 mJ, 10 ns pulse width and 1 Hz repetition frequency were used to ablate the target. The target was rotated with constant speed to ensure uniform ablation. The chamber was kept at a base pressure of (2×10^{-4}) torr.

Spectral analysis of optical transmittance and reflectance were recorded in the spectral range of 200-800 nm. As a function of different parameters: laser wavelengths, laser energy, number of pulses and target-to-substrate distances the study showed systematic changes that correspond to the thin films nanostructures. Moreover, a using available mathematical model deduced the refractive index, the extinction coefficient, and the measured data of the experimental transmittance spectra were fitted with the Cauchy's equation.

The energy dependent absorption coefficient was calculated from optical spectra to determine the bandgap (E_g). It was found that when target-to-substrate distance increases, the bandgap increases with a decrease in the confined dimension of the nanostructures a bandgap widening due to the quantum confinement effect.

The photoluminescence (PL) measurements showed visible light emission in the range 400-800 nm from synthesised silicon nanoparticles. The results clearly demonstrate that the PL band at ~1.8 eV is due to the quantum confinement effect (QCE) in the Si nanocrystal core, while the PL band at 2.5-2.8 eV is related to localized surface states at the Si/SiO_2 interface.
The Raman spectrum obtained shows that the deposited material is amorphous; the Raman spectrum is characterized for two faint and broad bands at (150 cm\(^{-1}\)) and (480 cm\(^{-1}\)). From X-Ray Diffraction (XRD) analysis and fixed Raman spectroscopy, it was confirmed that silicon samples nanoparticles are amorphous in nature.

Surface analysis by atomic force microscopy (AFM) showed that the morphology of the deposited films is nanostructured and demonstrated that the variation of laser energy from 0.3 to 500 mJ results in an average roughness at the surface changing from 8.9 to 20.8 nm whereas at 600 mJ the average roughness become 7.3 nm. Furthermore, analysis of the film topography with scanning electron microscopy (SEM) images show a mixture of nanoparticles and droplets due to the melting and evaporation processes, revealed that PLA of Si nanoparticles at (1064 nm) results in films with the roughest surface and the best crystallographic properties. At the same time, the films prepared at (532 nm) have the smoother surface but are of almost completely amorphous structure because of laser wavelength 1064 nm line penetrates deeply into the target, leading to a tremendous temperature rise in a large volume of the material.
1.1 Introduction

Nanoparticles are constituted of several tens or hundreds of atoms or molecules and can have a variety of sizes and morphologies (amorphous, crystalline, spherical, needles, etc.) [1].

The term “nanoparticle” itself may well conjure up an image of some amazing new contribution to the world of science from the realms of new materials technology. The potential impact of nanotechnology stems directly from the spatial and temporal scales being considered: materials and devices engineered at the nanometer scale imply controlled manipulation of individual constituent molecules and atoms in how they are arranged to form the bulk macroscopic substrate. This, in turn, means that nano-engineered substrates can be designed to exhibit very specific and controlled bulk chemical and physical properties as a result of the control over their molecular synthesis and assembly. It should be appreciated that nanotechnology is not itself a single emerging scientific discipline but rather a meeting of traditional sciences such as chemistry, physics, materials science, and biology to bring together the required collective expertise needed to develop these novel technologies [2].

Semiconductor nanocrystals having analogous interior bonding geometries compared to that of their known bulk counter parts exhibit distinct variations in their electrical and optical properties with size variation. The main reason for these changes lies in the systematic transformation of the crystal’s density of states as a function of energy, which varies as function of the nanoparticle sizes. From a density of states perspective, nanocrystals lie between discrete atomic and bulk “continuous band” limit. In any material,
there will be a size below which one observes a fundamental shift in electronic and optical properties as a function of size [3].

Nanoparticles effectively build a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties belong to its size, but at nanoscale a number of changes occur. Two of the major factors are the increase of the ratio of surface area to volume, and the size of particle moves into the range where quantum effects predominate. Particles with diameters between 0.1 and 1.0 μm are known as fine particles and normally consist of $10^9$ to $10^{10}$ atoms. Particles with these sizes are expected to exhibit solid state properties modified by the quantum effect [2].

Nanostructured materials have attracted a great deal of attention in the last decade for their unique characteristics that cannot be obtained from conventional macroscopic materials. Owing to quantum size effects, nanoparticles can display novel optical, electronic, magnetic, chemical, and structural properties that might find many important technological applications. An extremely active and prolific field in nanomaterials is finding ways to control size and morphology of the nanoparticles since the properties and applications of the nanoparticles are largely dependent on their size and morphology. The most evident manifestation of properties is the optical light emission in the blue-red spectral region characterized by a blue shift at smaller crystallite dimensions [4].

The optical and electrical properties of such organized nanocrystal solids could be tuned through nanocrystal size as shown in Figure (1-1) [5].
Due to the reduced size of their constituent elements, nanostructured materials have electronic, magnetic and chemical properties, which differ considerably from those of the corresponding bulk materials. For example, nanostructured materials have been found to exhibit increased strength and hardness, higher electrical resistivity, enhanced diffusivity, reduced density, etc. compared to the bulk. Hence, these materials are promising candidates for a variety of applications, which include heterogeneous catalysis, gas sensor technology, microelectronics, nonlinear optics, etc.

Depending on the size range, shape and chemical composition of nanoparticles, different techniques have been used for producing of such samples. Among them are wet chemical processes, physical methods and combined techniques. The ultimate goal of each technique is a fabrication of nanoparticles with a predetermined size and shape [6].
1.2 Literature Survey

The literature survey in the field of interest can be summarized as follows:

J. Levoska et al. (1999)

Pulsed laser deposition with an off-axis geometry in low-pressure argon ambient was used to produce films of nanosized silicon clusters or crystallites. Nanocrystals were obtained in the size range of 1-5 nm, measured by Raman spectroscopy. The nanocrystal size on the off-axis placed substrate was found to increase with increasing distance from the target, which made it possible to use it as a size selection method. The surface morphology of the deposits was studied using scanning electron microscopy. Weak room temperature photoluminescence of the samples with 514.5nm excitation was also observed [7].

J. L. Yeh et al. (1999)

It is found that a Si nanocluster could be formed in an amorphous silicon (a-Si) thin film following irradiation using a pulsed KrF excimer laser. The photoluminescence spectrum of the irradiated 70nm thick a-Si film at an energy density of 180 mJ/cm² at one shot shows two luminescence bands centered at ~1.31 and 1.76 eV. The peak emission wavelength depends on the silicon nanocluster size; which is ~3-4 nm [8].

M. H. Wu et al. (2001)

Silicon nanocrystals have been fabricated by picosecond pulsed laser ablation. They have studied the effect of different preparation parameters such
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as laser fluence, laser wavelength, backing gas pressure and distance from plume center on nanoparticle sizes. They found that nanocrystal size can be controlled by varying the laser pulse energy and the distance away from the center of the plume. Measurements of optical absorption and photoluminescence confirm that particle size variation significantly affected bandgap and emission efficiency [9].

J. H. Kim et al. (2002)

Nanocrystalline Si (nc-Si) on p-type Si substrate has been fabricated by pulsed laser deposition (PLD) technique using a Nd:YAG laser with different wavelengths of 355, 532, and 1064 nm. Pressure was maintained at $1\times10^{-5}$ Torr. Si nanocrystalline thin films were fabricated in 1–3 Torr He ambient. After deposition, nc-Si has been annealed in $N_2$ gas. Strong violet luminescence from Si nanocrystallites was observed at room temperature by photoluminescence (PL). Its peak energies shifted to green when the wavelength of pulsed laser was increased from 355 to 1064 nm. As the environmental gas pressure increased, weak green and red emissions from annealed nc-Si was also observed by PL [10].


Silicon nanocrystal films obtained by PLA in vacuum have PL spectra with a relaxation time of nanoseconds lie in the energy range 1.4-3.2 eV with a peak at 2.4-2.8 eV. At the longest times of tens of microseconds, the spectra become narrower, with a peak at 1.6 eV. Two bands are observed: low-energy (1.6 eV) and high-energy, with the peak shifting from 2.7 to 2.1 eV with time increasing [11].
T. Seto et al. (2003)

Silicon nanoparticles were fabricated by pulsed laser ablation in helium background gas. The size distribution of the silicon nanoparticles in the gas phase was controlled and measured by the electrostatic size classification technique using a differential mobility analyzer coupled with an electrometer. The microstructures and crystallinity of the as-deposited and size-classified nanostructured films were analyzed by scanning electron microscopy and Raman spectroscopy, respectively. The results of SEM were in reasonable agreement with the size distribution of the nanoparticles measured by theoretical model [12].

T. Makino et al. (2004)

The structural and optical properties of silicon (Si) nanoparticles (np-Si) prepared by pulsed laser ablation (PLA) in hydrogen (H₂) background gas. The mean diameter of the np-Si was estimated to be approximately 5nm. The infrared absorption corresponding to Si–Hₙ (n = 1, 2, 3) bonds was observed at around 2100cm⁻¹, and a Raman scattering peak corresponding to crystalline Si was observed at around 520cm⁻¹. The bandgap energy of np-Si prepared in H₂ gas (1.9 eV) was larger than that of np-Si prepared in He gas (1.6 eV) even though they were almost the same diameter [13].

M. H. Wu et al. (2005)

Silicon nanoparticles have been produced by picosecond pulsed laser ablation in vacuum at lower energy density. Nanometer-sized Si particles with average sizes ranging from 1-5 nm were collected on both crystalline and glass substrates. Nanoparticle size can be tuned through variation of the laser pulse energy density and by distance of the collection area from the plume
center. Raman spectra of the particles confirmed the crystalline nature of the nanoparticles and exhibited significant shifts due to phonon confinement effects. Optical absorption spectra of Si nanoparticles showed absorption edge ranging from 1.7 to 3.0 eV [14].

**J. H. Kim et al. (2005)**

The optical and structural properties of the films have been investigated as a function of deposition temperature, annealing, and oxidation process. When the deposition temperature increased, photoluminescence (PL) intensity abruptly decreased and peaks showed red shift. Annealing process can reduce the number of defect centers. Oxidation has considerable effects upon the formation and isolation of the nanocrystals [15].

**X. P. Zhu et al. (2005)**

Room temperature photoluminescence (PL) spectra for the Si nanoparticles were registered in blue-green range. The average crystal size (around 20nm) estimated from glancing angle X-ray diffraction (GAXRD) was relatively large, inconsistent with quantum size effect for the light emission [16].

**C. Grigoriu et al. (2005)**

Photo and cathodoluminescence of Si/SiO₂ nanoclusters produced by laser ablation was conducted. The study was made on untreated nanopowders (size 2–10 nm, 64% of primary nanoparticles < 5 nm), aged 18 months in normal atmospheric conditions. Photoluminescence spectra at room temperature and 77 K revealed a broadband spectrum (two bands 1.8 and 2.5 eV) in an approximate range from 400nm to more than 800 nm. The
maximum PL intensity measured at room temperature (RT), was centered at ~ 690 nm. At 77 K the photoluminescence emission peak increased by a factor of 3, and intensities for shorter wavelengths increased too (the luminescence color changed from red to orange) [17].

**D. Riabinina et al. (2006)**

Si nanocrystals embedded in a silicon oxide matrix were synthesized using reactive PLD followed by a post annealing treatment. This growth technique offers a great flexibility for tuning the nonoxidized Si concentration over a wide range (from 0.6 % to 64 %) by simply varying the oxygen pressure (from 1.5 to 0.03 mTorr). It was found that the variation of nonoxidized Si concentration results in a change in the nanocrystal size from 2.6 to 13.3 nm [18].

**S. Amoruso et al. (2006)**

The process of laser ablation of silicon targets with ≈1 ps/1055 nm and ≈100 fs/780 nm laser pulses has been investigated by exploiting optical emission spectroscopy and fast photography of the ablated species in the gas phase, and atomic force microscopy of less than one layer deposits of the ablated material. Whichever the nature of the target material, silicon or nickel, laser ablation of solid targets leads to the generation of an ablation plume composed of a fast plume component formed by atoms and ions of the target material, which expands at typical velocities of ≈10^6 cm/s or larger, followed by a much slower component of nanoparticles of the target material, characterized by a center–of–mass expansion velocity along the normal to the target surface of the order of 10^4 cm/s [19].
N. G. Semaltianos et al. (2008)

The debris produced by femtosecond laser ablation (180 fs, 775 nm, 1 kHz) of Si in ambient air is deposited around the ablated craters in a circular zone with diameters between ~40 and 300 μm for laser fluences (F) in the range F=0.2–8 J/cm$^2$. The debris consists of nanoparticles with mean height of the nanoparticles increases with laser fluence (from ~70 to 500 nm for fluences in the range F=0.25–4.38 J/cm$^2$) but at high fluences (F=8 J/cm$^2$) the height became equal to ~170 nm. The average horizontal dimension of the nanoparticles increases with laser fluence. Their average vertical dimension increases in proportion to their average horizontal dimension, but at high fluences they became much smaller than their corresponding average horizontal dimension [20].

C. Meier et al. (2008)

Quantum size effect was observed in the photoluminescence for nanoparticles with diameters below 10 nm. Moreover, when cooling the sample from 300 to 80 K, the PL intensity increases first, reaches a maximum at $T \approx 80$ K and then decreases again when the temperature was decreased further. This is different from what is observed in most other semiconductor quantum dots or nanocrystals made from direct semiconductors [21].

V. Švrček et al. (2009)

Stable and blue-luminescent Si-ncs was produced by laser generated plasma (nanosecond-pulsed excimer laser) confined in water. These Si-ncs exhibited quantum confinement effect due to their size and were produced with an environmentally compatible process. The effect of aging for several weeks in water and air on blue emission properties was investigated [22].
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1.3 Aims of the Research

Aims of this study are summarized as follow:

A. Producing silicon nanoparticles by the laser ablation technique, studying the effects of the affective parameters on the deposited film features, and controlling the silicon nanoparticles features (size, density and photoluminescence emission).

B. Conducting some the experimental measurements: optical and morphological properties to characterize the deposited films.

1.4 Silicon nanostructures

Silicon is the leading material concerning high-density electronic industries. Nanostructuring silicon is an effective way to turn silicon in to a photonic material. The small size results in new quantum phenomena that yield some extra ordinary bonuses. Material properties change drastically in the nanoscale because quantum effects arise from the confinement of electrons and holes in the material. Moreover, at nanoscale short rang forces such as Van der Waal forces predominate [3].

The most important motivation to the study of nc-Si was the hope to get luminescent silicon. In fact, silicon has an indirect bandgap, which causes a very long radiative lifetime (ms) for excited electron-hole pairs. Competing non-radiative recombination's prevail and cause most of the excited electron-hole pairs to recombine non-radiatively. In addition, when the number of excited electron-holes increases other non-radiative recombination processes start to play a role [23].

The recombination does not need the participation of a third particle. The radiative lifetime $\tau_{\text{rad}}$ due to the band-to-band recombination in Si (equal
to about 10ms) is significantly slower than the radiative recombination for direct bandgap semiconductors, which is of the order of 100 ns. This means that different non-radiative de-excitation mechanisms, which strongly concur to suppress the band-to-band recombination, are in competition with the radiative recombination [24].

Unlike the II-VI and III-V materials, Si is a biocompatible semiconductor that is electrochemically stable. For indirect bandgap semiconductors like Si (Figure 1-2), the bottom of the conduction band and the maximum of the valence band occur at different wavevectors in the reciprocal space. With the decrease of the size of an indirect bandgap semiconductor, the bandgap energy increases and the energy bands become pseudo-continuous or split to discrete energy levels. Particles with sizes smaller than the Bohr exciton radius (ca. 4.3 nm for silicon) exhibit quantum confinement effect and thereupon, photoluminescence shifts to the visible of the electromagnetic spectrum.

Figure (1-2): Band structure of bulk Si with the various possible transitions for an electron-hole pair [23].
The radiative recombination rate in nc-Si may be with or without phonon mediated, depending upon the crystallites size and the nature of the nc-Si (presence of impurity states). As the crystallite size decreases, there is no phonon mediation because of the QCE (The Phonon participation decreases as the size of nc-Si decreases, because the band gap changes from indirect to direct due to QCE). The QCE changes the energy level spectrum in the bulk material into a discrete level structure namely the sub-band structure. This leads to the enhancement of the oscillator strength of the exciton through increased spatial overlap between the electron and holes [25]. The strong spatial confinement in the nc-Si implies that for the excitons created in the nc-Si, there is an increase in the radiative recombination rate of the radiative nc-Si. As a result, the quantum efficiency of the system increases. On the other hand, non-radiative recombination in the non-radiative nc-Si decreases and the quantum efficiency of this process goes to zero [26, 27].

The field of nanostructure physics has been growing rapidly in recent years, and much theoretical insight has been gained hand in hand with progress in experimental techniques and more device-oriented applications [28].

1.5 Low-Dimensional Structures (LDS)

Low-dimensional Structures (LDS) form a major new branch of physics research. These semiconductor structures have such a small scale in one- or two-dimensions that their electronic properties are significantly different from the same material in bulk form. These properties are changed by quantum effects [29].
A low-dimensional material is one where the motion of microscopic degrees-of-freedom, such as electrons, phonons, or photons, is restricted from exploring the full three dimensions of our world. There has been tremendous interest in low-dimensional quantum systems during the past twenty years.

The study of low-dimensional quantum phenomena has led to entirely new fields of research, such as the physics of mesoscopic systems [30].

1.6 Density of States (DOS)

The advantages in operation depend not only on the absolute size of the nanostructures in the active region, but also on the uniformity of size. A broad distribution of sizes "smears" the density of states, producing behavior similar to that of bulk material [31].

As a result of quantum confinement in different directions, there is a change in the wave function describing the behavior of electrons and holes, and consequently also the number of states per unit energy, i.e., the density of states (DOS), changes as a function of the energy E of the particle. On the other hand, the arrangement of the atomic bonds at the surface also strongly affects the energy distribution of electronic states, since in Si-nc the silicon atoms are at the surface or few lattice sites away. Figure (1-3) gives the schematics of the low dimensional structures.
Since the density of states as a function of energy varies with a transition from the atomic to bulk crystal regime, it logically follows that both optical and electronic properties depend strongly on nanocrystal size [3].

### 1.6.1 Density of states for bulk materials

The effective mass equation for carriers in bulk semiconductors in the envelope-function approximation.

$$\left[ -\frac{\hbar^2}{2m^*} \nabla^2 + V(r) \right] C(r) = (E - E_i(r))C(r) \quad (1-1)$$

Here, $C(r)$ is the envelope function of carriers in the band under consideration. The Schrödinger equation is thus re-cast in a form which is identical to that of
an electron in a total potential \( V(r) + Ec(r) \), determined by the band-edge behavior.

and energies

\[
E(k) = E_{c0}(r) + \frac{\hbar^2 k^2}{2m}\;=\;E_{c0}(r) + \frac{\hbar^2}{2} \left( \frac{k_x^2}{m_{xx}} + \frac{k_y^2}{m_{yy}} + \frac{k_z^2}{m_{zz}} \right)
\]

\( E_{c0} \) is a constant energy (flatband conditions), one should not forget that even though \( k \) is written as a continuous variable, they are actually quantized, assuming values

\[
k_x = k_y = k_z = \frac{2\pi}{L} m
\]

(1-3)

Where \( m = 0, \pm 1, \pm 2, \ldots \). Since \( L \) is a macroscopic length, the quantization is very fine, and for all practical purposes, \( k \) can be assumed continuous.

The density of states (DOS) is given by [32]

\[
g_{3D}(E) = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_{c0}}
\]

(1-4)

1.6.2 One-Dimensional Quantum Systems (Quantum Wires)

Artificial quantum wires (QWRs) are formed either lithographically (top-down approach), or by direct growth in the form of semiconductor nanowires or nanotubes (bottom-up approach). In a quantum well (QW), out of the three degrees of freedom for real space motion, carriers are confined in one, and are free to move in the other two. In a quantum wire, electrons are free to move freely in one dimension only (hence the name ‘wire’), and the other two degrees of freedom are quantum-confined. Assume that the length of the wire (total length \( L_z \)) is along the \( z \)-direction, figure (1-4), and the wire is quantum-confined in the \( x-y \) plane \( (L_x, L_y \ll L_z) \). [32]
the energy eigenvalues are given by

\[ E(n_x, n_y, k_z) = E(n_x, n_y) + \frac{\hbar^2 k_z^2}{2m_{zz}^*} \]  

(1-5)

If the confinement in the x-y directions is by infinite potentials (a useful model applicable in many quantum wires), then similar to the quantum well situation, a wave-fitting procedure gives

\[ k_{nx} = \frac{\pi}{L_x} n_x, \]  

(1-6)

\[ k_{ny} = \frac{\pi}{L_y} n_y, \]  

(1-7)

Where \( n_x, n_y = 1, 2, 3 \ldots \) independently.

and the corresponding energy band structure is given by

\[ E(n_x, n_y, k_z) = \left[ \frac{\hbar^2}{2m_{xx}} \left( \frac{\pi n_x}{L_x} \right)^2 \right] + \left[ \frac{\hbar^2}{2m_{yy}} \left( \frac{\pi n_y}{L_y} \right)^2 \right] + \frac{\hbar^2 k_z^2}{2m_{zz}^*} \]  

(1-8)

Multiple subbands are formed, similar to the quantum well structure. A new subband forms at each eigenvalue \( E(n_x, n_y) \), and each subband has a dispersion

\[ E(k_z) = \frac{\hbar^2 k_z^2}{2m_{zz}} \]  

(1-9)
The DOS of electrons confined to an ideal 1-D potential is given by

\[
g_{1D}(E) = \frac{1}{\pi} \sqrt{\frac{2m^*}{\hbar^2}} \frac{1}{E - E_1}, \quad (1-10)
\]

Where \(E_1\) is the lowest allowed energy (ground state).

The general DOS for a quantum wire can thus be written as

\[
g_{QW}(E) = \frac{1}{\pi} \sqrt{\frac{2m^*}{\hbar^2}} \sum_{n_x, n_y} \frac{1}{\sqrt{E - E(n_x, n_y)}}, \quad (1-11)
\]

Which is shown schematically in Figure (1-4).
1.6.3 Two-Dimensional Quantum Systems (Quantum Wells)

Quantum wells are formed upon sandwiching a thin layer of semiconductor between wider bandgap barrier layers. The finite extent of the quantum well layer makes the conduction band profile one-dimensional quantum well in the direction of growth (z-direction), leaving motion in the x-y plane free [32].

The DOS of the quantum well is

\[ g_{qw}(E) = \frac{m^*}{\pi \hbar^2} \sum_{nc} \theta(E - E_{nc}) \]  

(1-12)

Where \( \theta \) is the unit step function as shown in Figure (1-5).
1.6.4 Zero-Dimensional Quantum Systems (Quantum Dots)

The quantum dot is the ultimate nanostructure. All three degrees of freedom are quantum confined; therefore, there is no plane-wave component of electron wavefunctions [32].

![Figure (1-6): Energy levels and DOS of quantum dots (QDs) [32].](image)

The energy eigenvalues in this system are no more quasi-continuous, and are indexed by three quantum numbers \((n_x, n_y, n_z)\). Thus, it does not make sense to talk about “band structure” of quantum dots; the DOS is a sum of delta functions, written as

\[
g_{QDot} = \sum_{n_x, n_y, n_z} \delta(E - E_{n_x, n_y, n_z}), \tag{1-13}
\]

This is shown schematically in Figure (1-6). Since there is no direction of free motion, there is no transport within a quantum dot, and there is no quasi-continuous momentum components.
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1.7 Quantum Confinement

Quantum confinement in nanostructures of indirect gap semiconductors has attracted great interest due to the changes in the electronic structure of these materials, which significantly enhance their luminescence efficiency. After the first observation of visible photoluminescence (PL) from Si nanocrystals (Si-nc) at room temperature, nanostructured semiconductors such as porous Si, Si nanoparticles, Si nanocrystals embedded in silicon oxide, and Si/SiO$_2$ superlattices have been intensively studied because of their potential optoelectronic applications [18].

Quantum confinement effects in semiconductor nanoparticles were discovered more than two decades ago and have attracted increasing interest during recent years. Influence of particle size on the energy levels of excitons and conduction band edges were verified for a variety of nanoscaled materials, e.g. small structures of silicon, germanium and indium phosphide. In the field of nanotechnology, applications such as quantum dots and quantum wires were developed, depending on the dimensionality of the spatial boundary conditions. Confined structures are characterized by a sharper density of states compared to higher-dimensional objects, which plays an important role in the design of a multiplicity of devices like diode lasers, biological sensors and solid-state quantum computers. In addition, quantum confinement is revealed by a blue shift of energy levels with decreasing particle size [33].

The emission of visible light, instead of the 1.1μm wavelength characteristic of bulk Si, has been ascribed to quantum confinement effects. For nanometric Si clusters, the classical physics of matter results inadequate to describe the light emission phenomenon. The classical representation of e-h pairs, forming the exciton, should be replaced with the description in terms of
wave functions related to electrons and holes, confined in a potential box, whose size is D. This increase in ground state energy is referred to as confinement energy or quantum confinement. Due to this increase, the overall bandgap in the quantum confined particle widens with respect to the bulk crystal. Or in another words, due to the reduced size of the particle, it can be described as potential well. With decreasing size of the potential well, the ground state energies are increased, resulting in a shift of the band edges, and an overall opening of the bandgap [24].

![Figure (1-7): Basic concept of quantum confinement in silicon nanostructures [24].](image)

If we confine the electron hole pairs (excitons) in a small region, having dimensions of the order of a few nanometers, the properties of the material completely change. Since the order of magnitude of the electron and hole de-Broglie’s wavelength (~1nm) is comparable with the confinement dimensions, they behave as particles in a box and the problem can be solved by quantum mechanics. Consequently, the confinement effect in a region of nanometric size is referred to as quantum confinement effect, and the physical structure, in which the quantum confinement of excitons occurs, is termed as a nanostructured material.
Most of a material’s behaviors, such as intrinsic conductivity, optical transitions and electronic transitions, depend on the energy-gap between the conduction band (CB) and the valance band (VB). Any change of the gap may significantly alter the material’s physical and chemical properties. Miniaturizing a semiconductor for instance down to a nanometer scale causes the bandgap ($E_g$) to expand and the inner core level to shift towards higher binding energy. The dielectric constant ($\varepsilon_r$) of the semiconductor is no longer constant but decreases with solid size. The reduced ($\varepsilon_r$) has enormous impact on the electrical and optical performance of the solid and the related devices [34]. It is generally agreed that quantum confinement caused by the restricted size of the nanometer scale silicon particles is essential for the light emitting properties [35].

The quantum size effect predicts the formation of a bandgap with decreasing particle for metals, and widening of the intrinsic gap for semiconductors.

Silicon nanocrystals, for instance, are complex systems and several models have been proposed in order to describe their band structure. The simplest model used to describe the bandgap in such nanostructures or quantum dots is the effective mass approximation (EMA).

There is non-negligible amount of negative Coulombic attraction between the electron and its associated vacancy (hole). Although free excitons are free to move about the crystal as an e-h pair, as long as sufficient optical excitation continues the electron and the hole will both be mutually bound. That is, free electrons are still bound as e-h pairs. Of course, there is a natural
spatial e-h separation most desired by the system. In the EMA approximation, this separation used to establish the presence of quantum confinement effect, is the Bohr radius of the exciton. This may be easily calculated by balancing the central force on the electron \((m_0 v^2/r_n)\) to the Coulombic attraction force.

\[
\left( \frac{q^2}{4 \pi \varepsilon_r r_n^2} \right) \]

i.e., \(\frac{m_0 v^2}{r_{\text{ex}}} = \frac{q^2}{4 \pi \varepsilon_r \varepsilon_o r_{\text{ex}}^2}\) \hspace{1cm} (1-14)

Quantum confinement effects arise if the Bohr radius of the exciton is affected by the spatial boundary conditions of the host particle when reaching a critical size. Its deformation increases with decreasing particle size and is revealed by an increasing energy of the exciton [33].

Via the Bohr postulate, the angular momentum \(L\) may be expressed as \(m_0 v r_n = n \hbar\) It follows then;

\[
r_{\text{ex}} = \frac{4 \pi \hbar^2 \varepsilon_r \varepsilon_o}{\mu e^2} \hspace{1cm} (1-15)
\]

Where \(\mu\) is the reduced mass of the exciton, \((e)\) is the electric charge of the electron, \((\varepsilon_r)\) is the relative dielectric constant of Si, \((\varepsilon_o)\) the dielectric constant of vacuum and \((\hbar)\) is plank’s constant.

The significance of the excitonic Bohr radius is that it provides a threshold value below which the confinement regime becomes relevant. Effective mass approximation can be illustrated by a simple case of
confinement in a nanocrystal with linear dimension \( L_x, L_y, L_z \) where the bandgap is given by the expression:

\[
E_{nc} = E_{g\text{ Si[bulk]}} + \frac{\hbar^2 \pi^2}{2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)
\]  

(1-16)

Where \( E_{g\text{ Si[bulk]}} = 1.12 \text{ eV} \), while and \( m_e^* \) and \( m_h^* \) are respectively the effective mass of electrons and holes. According to this expression, it is evident that the energy necessary to generate an electron-hole pair increases by decreasing the size of the system. Theoretical calculations of the band-gap widening have been confirmed experimentally by absorption measurements. Figure (1-8) illustrates the calculated bandgap variation with a decrease in size of the particles.

![Figure (1-8) Calculated band gap energies for Si-crystals depending on their diameter [36]](image)

The quantum confinement determines the enlargement of the bandgap and leads to the breakdown of the momentum conservation rule, allowing no-
phonon optical transitions (like in the case of a direct gap), but its main contribution consists in the appearance of new energy levels [37].

1.8 Band Structure Calculations

Different theoretical and experimental works have been carried out in order to explain the size dependent properties of semiconductor nanocrystals. These works are primarily based on the Effective Mass approximation (EMA) method, Empirical Pseudopotential Approach (EPA), and Tight-Binding Scheme.

1.8.1 Effective Mass Approximation (EMA)

The idea of the effective mass theory is that the effect of the periodic field in a crystal can be replaced by an effective electron (hole) mass tensor \( m^* \). The general Hamiltonian in the effective mass approximation becomes

\[
H = -\frac{\hbar^2}{m^*} \nabla^2 + V(x) \quad (1-17)
\]

With \( m^* \) being the effective mass tensor and \( V(x) \) being some outside potential. This very basic approach is limited to the cases where the relevant band has its extremum at the center of the Brillouin zone.

The energy gap \( E_g \) of the Si cluster depends on the physical size because of the carrier confinement, when the diameters become less than the free-exciton Bohr radius (~5nm). This implies that energy gaps are useful indicators for discussing the physical structures of probeinduced defects.
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The idea of effective size parameters is helpful in comparing with Si nanostructures with different shapes. Zunger and Wang [38], proposed an effective diameter $D_{eff}$, which was defined by the diameter of a sphere that had the same volume as a different-shaped structure. $D_{eff}$ is given by

$$D_{eff} = 0.794D \text{ (nm)} \quad (1-18)$$

for the hemispherical shape of a cluster.

**Effective mass approximation (EMA),** as proposed, has been used to explain the change of energy gap as a function of particle size. According to EMA, the equation derived for radius of particle is given by [39]

$$\Delta E_g = E_{g(Film)} - E_{g(bulk)} = \left[ \frac{\hbar^2}{8\mu r^2} \right] - \frac{1.8e^2}{\varepsilon_r \varepsilon_r r} \quad (1-19)$$

Where $\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$ is the reduced mass of electron hole effective mass, $m_e^* = 0.34m_o$ and $m_h^* = 0.23m_o$, and $\varepsilon_r = 8.76$ is the permittivity of the sample [4].

The energy gap $E_g$ of the Si cluster by using an empirical pseudopotential calculation, is expressed as [39]

$$E_g = 1.17 + 3.3D_{eff}^{1.37} \quad , \quad (1-20)$$

Where 1.17 corresponds to the energy gap of bulk crystalline Si. **Tight-binding** calculation were approximately consistent with this curve, so that Eq.
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\[ E_g = 1.6 + 0.8D_{\text{eff}}^{-2} \]  
\( (1-21) \)

The fitted energy gap of 1.6±0.4 eV and exponent of 2±0.5 are approximately consistent with those reported on amorphous Si clusters expressed as [39]

\[ E_g = 1.56 + 2.4D^{-2} \text{ (eV)} \]  
\( (1-22) \)

This result suggests that the deposited Si clusters contain disordered structures. On the other hand, the fitted confinement parameter of 0.8±0.4 is smaller than that of the amorphous Si clusters, indicating the reduction of electron and hole effective masses. We consider that the surface states around the clusters reduce the effective masses.

1.8.2 Pseudopotential Model

In a crystal, the valence electrons away from the ions behave as nearly free electrons in a periodic Coulomb potential.

The concept of the pseudopotential method is to divide the valence wave functions into a smoothly varying part (pseudowave) outside the core regions and an oscillatory part near the core region. The oscillatory part can then be replaced by an "effective" weak potential acting on the valence electrons. The combination of this effective core potential and a screened ion potential is called the pseudopotential. A schematic plot of the pseudopotential Figure (1-9).
The valence pseudowave function is then in essence the true valence wave function minus the core states and satisfies the Schrödinger equation.

There are two basic approaches to calculate band structures with the pseudopotential method: the empirical pseudopotential model (EPM) and the self-consistent or *ab initio* method. The EPM requires some experimental input to determine the pseudopotentials whereas the self-consistent method models the potentials. The relevant theoretical work for nanocrystals is based on the empirical approach, which also in general yields more accurate results for band structures.

This approach yields single-particle gaps. Based on the ground-state solution, excitonic states with an electron in the conduction band and a hole in

Figure (1-9): Schematic of the pseudopotential model [4].
the valence band can be calculated. The coulomb interaction between the electron and the hole is screened with a nanoparticle size dependent dielectric screening function. With this method, excitonic gaps can be calculated.

1.8.3 Tight Binding Model

The tight-binding model takes an opposite approach to the pseudopotential model to describe the electronic structure in a crystal. While in the pseudopotential model, the electrons are assumed to be nearly free and their wave functions can be approximated by plane waves, the tight-binding model assumes the electrons to be concentrated in the bonds between the atoms.

The tight-binding (TB) model has become a popular and convenient tool for total energy calculations and molecular dynamics simulations of complex systems. It offers a reasonable compromise between classical interaction potentials and \textit{ab initio} electronic structure calculation methods, being rather close in efficiency to the former due to strong simplifications in the electronic structure calculations [41,42].
1.9 Nanostructure Preparation Techniques

The methods of manufacturing silicon nanostructures are very diverse such as the chemical anodization, plasma enhanced chemical vapor deposition (PECVD), ion implantation, laser etching and the manufacture of thick SiO_x films (oxidation). For real technological utilization, it is required that the density, size, and position of the nanocrystals should be controlled independently [43].

These techniques can be divided into three main approaches: direct synthesis of silicon clusters, formation of a silicon reach layer and subsequent thermal induced phase separation and electrochemical erosion of bulk silicon. Figure (1-10) gives schematics of some of these techniques [3]:

![Diagram of silicon nanocrystal fabrication techniques](image-url)
1.9.1 The etching process

Many etching techniques have been developed to produce porous silicon by a chemical reaction on the silicon surface.

A. Electrochemical Etching of Silicon

Porous Silicon (P-Si) is obtained by the electrochemical etching of crystalline silicon (C-Si) in Hydrofluoric Acid (HF) rich electrolyte [44]. Following the partial wafer dissolution, a porous silicon structure is formed where the silicon skeleton is either by interconnected nc-Si or by thin silicon wires. The etching process is self-regulated. Once the porous layer formed, no further etching of porous layer occurs. The reason for this is the depletion of holes in the etched region of the samples. The anodic current has to be less than the electro-polishing current, above which electro-polishing of the silicon occurs and the final layer has mirror like nature without any porous silicon in it [45].

![Schematic of the electrochemical anodization system to fabricate nanocrystalline porous silicon layer](image)

Figure (1-11): schematic of the electrochemical anodization system to fabricate nanocrystalline porous silicon layer [45]
B. photochemical etching:

Laser-induced etching has been used to produce porous silicon (PS) and nanocrystallites of silicon. This technique opens new possibilities of precise patterning for large-scale integrated circuits and silicon-based optoelectronics. In laser-induced etching, when an n-type Si wafer is immersed in aqueous HF acid and illuminated with laser light, a large number of electron–hole pairs are generated in crystalline-silicon (c-Si) in the irradiated area. A fair percentage of both charges will diffuse rather than immediately recombine due to the indirect bandgap in silicon. Furthermore, because of the internal field caused by band bending, holes are driven into the surface to initiate the etching process [46].

Figure (1-12): Schematic diagram of Laser-induced etching process [47].

1.9.2 Nano-Silicon Produced by Phase Separation

This method is the most widely used. Various techniques have been employed in this technique. Ion implantation, plasma enhanced chemical vapour deposition (PECVD), and Sputtering, produces nc-Si [48]. The
difference among them is related to the degree of purity of the film. The purity of nc-Si produced by ion implantation is better than the other techniques.

A. The Sputtering

In sputtering, a target held in a partial vacuum (from a few mTorr to around a 100 mTorr) is eroded by a stream of ions of an inert gas, usually argon, which dislodges material from the target surface by collision. The target is negatively biased; to the order of several kilovolts using a DC or RF power supply, so that it acts as a cathode, causing the gas to breakdown and form discharge plasma. The positive ions created are attracted to the cathode, causing neutral target ions to be ejected with energies in the range $E \sim 2$-$30$ eV, much higher than that for thermal evaporation. The substrate is placed facing the target. It may also have a positive or negative bias, be heated or cooled depending on the type of film to be grown. This discharge allows current to flow and a film condenses on the substrate anode since the neutral atoms may traverse the discharge region. In addition, negatively charged ions produced at the target surface are accelerated into the growing film, aiding densification [48].

B. Aerosol technique

Here Si-nc are formed and dispersed in a carrier gas flow where they may undergo oxidation processes or also size selection by precipitation [3].

C. Ion-implantation

Si-nc can be produced by implanting silicon ions fired at a piece of a bulk material. As the ions pass into the sample they initially lose energy by exciting the electrons of the atoms they pass, which is a relatively non-
destructive process. However, when sufficient energy is lost, they will begin to collide with the atomic nuclei along their trajectory causing the atoms to be displaced. Since the ions may have travelled microns into the surface before this occurs this means that the immediate surface region is left relatively unscathed whereas the stopping region will show appreciable disorder (or in the crystalline case may even become amorphous). When high temperature annealing is followed, it will induce precipitation and forms the nc-Si [48].

D. PECVD technique:

This technique is fully compatible with the Si very large-scale integration (VLSI) technology and recently it has been shown that PECVD of sub-stoichiometric silicon oxide (SiO$_x$) layers followed by high temperature annealing represents a quite powerful method to produce Si-nc within SiO$_2$. PECVD allows the deposition of thin films by using an electric discharge to induce chemical reactions in a gas. The plasma is generated by the application of an RF field to a low pressure gas, thereby creating free electrons within the discharge region. The reactive species generated by the plasma are then adsorbed on the substrate surface, where they are subjected to ion and electron bombardment, rearrangements, reactions with other adsorbed species, new bond formations, leading to film formation and growth of nanostructure [3].

1.10 Laser ablation

In laser ablation, high-power laser pulses are used to evaporate matter from a target surface such that the stoichiometry of the material is preserved in the interaction. As a result, a supersonic jet of particles (plume) is ejected normal to the target surface. The plume, similar to the rocket exhaust, expands away from the target with a strong forward-directed velocity distribution of
the different particles. The ablated species condense on the substrate placed opposite to the target. The ablation process takes place in a vacuum chamber - either in vacuum or in the presence of some background gas. In the case of oxide films, oxygen is the most common background gas [49].

1.10.1 History of PLD

PLD in its first form was undertaken by Smith and Turner [50] who used a ruby laser to deposit thin films of a range of different types of material including semiconductors and chalcogenide glasses, from powder and crystal targets. However the limited number of suitable pulsed laser sources available at the time was, in retrospect, the main factor in ensuring that these films were inferior to those produced by other methods. This meant that research into PLD was sporadic, and little attempt was made to improve the film quality [48].

For short laser pulse, high peak power, Q-switched lasers became available interest in PLD was rejuvenated. These allowed power densities where congruent evaporation was possible. Congruent evaporation occurs when the temperature of the target surface is raised so rapidly by the incident pulsed that the target constituents evaporate simultaneously, and with the same rate, so that the evaporated plume maintains the stoichiometry of the target. This is one of the major strengths of PLD, since it is fundamental to the growth of materials with complex compositions. The higher kinetic energies of the species in the plume could utilize PLD in growing complex oxide films. This is due to the fact that ablated metal atoms form oxides with an oxygen containing background gas more readily when the kinetic energies are high [48].
1.10.2 Mechanism of Pulsed Laser Deposition

The principle of pulsed laser deposition, in contrast to the simplicity of the system set-up, is a very complex physical phenomenon. It does not only involve the physical process of the laser-material interaction of the impact of high-power pulsed radiation on solid target, but also the formation of plume with high energetic species and even the transfer of the ablated material through the plume onto the heated substrate surface. Thus, the thin film formation process shown schematically in Figure (1-13) can be divided into (at least) three steps:

1. Laser - target interaction
2. Plume expansion
3. Film deposition

Each process step is very material dependent as well as dependent on experimental parameters such as laser wavelength, laser fluence and pulse width, background gas type and pressure, substrate type and temperature, and deposition geometry [51].

Figure (1-13): Schematic presentation of the pulsed laser deposition process [51].
The time scales involved in the three process steps are very different. Typically, the laser-target interactions occur within nanoseconds (ns), whereas the plume expansion in a background gas takes place within microseconds (μs) [51]. Depending on the experimental conditions, the film growth process following a laser pulse can in principle continue to develop until the next laser pulse occurs milliseconds later.

A. Laser – target interaction

Since the laser power density on the target is above the threshold for plume creation, an expanding plume is formed above the target surface during ablation. This plume formation threshold is typically higher than the power density threshold for laser ablation.

When a pulsed high-power laser interacts with a target material, the process is often referred to as “laser ablation”. Here ”ablation” covers a variety of processes that occur during the interaction such as absorption, surface melting and vaporisation, ejection of particles, and plume formation and expansion [51-53]. The actual sequence of events which occurs when the laser pulse arrives at the target is illustrated in Figure (1-14). Firstly, a), the leading edge of the pulse causes the surface to melt. Then, b), the melt front proceeds further into the target as the molten material begins to evaporate. Then, c), a dense plume forms which is still opaque to the laser pulse causing its temperature to rise rapidly. Finally, d), this plume expands rapidly, becoming more transparent as the plume density decreases, the plume absorbs the laser radiation by inelastic free electron scattering also called inverse-
Bremsstrahlung, which results in further heating of the plasma. The molten material which is left behind then begins to resolidify [51].

![Figure (1-14): Schematic presentation of the laser target interactions during a High-power laser pulse [51].](image)

**B. Plume expansion**

In PLD, the plasma plume typically expands in a background atmosphere. However, in order to describe plume expansion in an atmosphere, some knowledge of plume expansion in vacuum is necessary. Firstly, plume expansion in vacuum with a high-power laser pulse of around 30 ns duration, a bubble of hot plasma could be formed ≤ approximately 50 μm from the target surface. As soon as the plasma is created, the plasma particles interact and tend to of the primary ablation mechanisms [51-54].
C. Film deposition

The film growth process or deposition of ejected target material onto a growing film, can be described by the following sequence: Firstly, the arriving particles must be adsorbed on the surface, then they may diffuse some distance before they react with each other at the surface and start to nucleate. The way the particles nucleate may determine the structure or morphology of the growing film. Under certain circumstances (high substrate temperature), diffusional interactions within the film and with the substrate, beneath the growing film surface, may subsequently modify film composition and film properties.

In PLD, film growth is highly influenced by the process parameters. In the following, some typical film growth modes will briefly be described and subsequently some PLD growth characteristics will be discussed. Finally, different film structures will be mentioned. The following subsections are mainly based on the references [55].

In general, three conventional modes of nucleation and growth are considered:

A. Three-dimensional island growth called Volmer-Weber growth.
B. Two-dimensional full-monolayer growth called Frank - van der Merwe growth.
C. Two-dimensional growth of full monolayers followed by nucleation and growth of three-dimensional islands called Stranski-Krastinov growth.
The selection of one of these growth modes by a substrate-film system depends on the thermodynamics that relates the surface energies (film and substrate) to the film-substrate interface energy.

**Volmer-Weber nucleation and growth**

Figure (1-15) illustrates the different processes involved in the nucleation of clusters on a surface by vapour deposition of atoms. The balance between growth and dissolution processes for a given cluster will be governed by the total free energy of a cluster, $\Delta G$, relative to an assemble of individual atoms. In general, for three-dimensional cluster growth, $\Delta G$ will have a maximum, $\Delta G^*$, at a critical cluster size, which means that cluster sizes above this critical size are stable [51,55].

To a first approximation, *the nucleation rate* is given as the product between the arrival rate of atoms at critical-size nucleus and the concentration of critical nuclei. The former is proportional to the concentration of mobile atoms on the surface and to the surface diffusion coefficient. The latter is a strongly decreasing function of $\Delta G^*$. As a rule, an increased cluster nucleation rate is desired in Volmer-Weber growth. In practice, this can be achieved by increasing the deposition rate (or decreasing the substrate temperature) which gives a decrease in $\Delta G^*$.

**Frank - van der Merwe nucleation and growth**

Full monolayer growth involves nucleation and growth of islands that are only one monolayer thick and grow to essential complete coalescence before significant clusters are developed on the next film layer. In this case there is no free energy barrier for nucleation (no $\Delta G^*$). If the surface material is different from the film material, full monolayer nucleation will be promoted
by strong film-substrate bonding, low film surface energy and high substrate surface energy.

Figure (1-15) Schematic diagram of atomic processes in the nucleation of 3-D clusters of deposited film atoms on a substrate surface [51].

Stranski-Krastinov nucleation and growth

Full monolayer growth may change to three-dimensional island growth after 1-5 monolayers due to a change in the energy situation with successive monolayers. This could be an increase in stress with increasing layer thickness due to mismatched lattice spacings [53].
1.11 Characteristic features of laser ablation deposition

Various features could be obtained by pulse laser ablation:

1. Films can be obtained from almost all kind of materials irrespective of their optical as well as thermal properties.
2. The target size or area required for laser ablation experiment can be quite small (~ 1 cm$^2$)
3. Due to the extreme rapidity of the evaporation and deposition process material is transferred from target surface to the substrate congruently.
4. High instantaneous growth rates of the order of several thousand angstroms of the depositing film thickness per second can be achieved.
5. The growth rate as well as the quality of the depositing film can be controlled by varying the different experimental parameters like power density of the incident laser beam, laser spot size on target surface, target to substrate distance and position of the substrate with respect to the laser spot on the target surface.
6. Laser ablation deposition experiments can be carried out in any atmosphere maintained inside the chamber and at any vacuum level with the required background gas atmosphere. This is not possible in case of other vapour deposition processes. For example, electron beam evaporation deposition needs a vacuum level of at least $10^{-4}$ torr. Further, the electron gun filament may corrode in a detrimental gaseous environment maintained inside the chamber.
7. Laser ablation technique can be similar (energetic) with other techniques like sputtering.
8. Experimental set-up for laser ablation is relatively simple.
On the other side, laser ablation has some limitations

1. Films of uniform thickness cannot be grown on a sufficiently large area of the substrate because of the highly forward directed nature of the vapour plume.
2. Because of the same reason in-situ thickness measurement of the film, growing on a substrate is not possible.
3. Deposition cannot be accomplished over a large area, again because of the directional nature of the deposition process.
4. Prolonged irradiation of the target surface by a laser beam makes the surface rough. As the surface becomes rough, more surfaces are created and the laser fluence on target surface decreases.
5. The laser ablation process has a serious problem in the fact that the films deposited by this technique have particulates of micrometer size embedded in it. These particulates have both spherical and irregular shapes. The spherical particulates come through the process of breaking or splashing of a thin liquid layer on the surface of the target irradiated with laser [56].

1.12 Properties of Silicon Nanoparticles

1.12.1 Optical Properties

Recently, a significant effort has been focused on the formation and characterization of Si nanocrystals (Si-nc), which can play a key role as an emission source (electroluminescent diodes and lasers) for silicon-based optoelectronic applications, even considering the fact that silicon is an indirect material with low emission efficiency. This is because of the spatial
confinement of excitons in small enough silicon nanoparticles, which leads to the delocalization of the wave vector \( k \) in reciprocal lattice and may then break the \( k \) selection rules, enhancing the probability of the indirect optical transition. Moreover, it has been already shown by many authors that indirect transition (or quasi-direct) will strongly depend on the size of nanocrystals and shift to higher energies due to the quantum confinement for small enough nanocrystals [57].

Properties of the direct optical transitions in Si-nc have not been extensively investigated thus far, experimentally. The issues related to their dependence on nanocrystal size and their importance in the absorption mechanism are still open questions [57,58]. It is mostly because many significant problems are unresolved thus far, such as the controversy concerning the Stokes shift between the absorption gap and the photoluminescence peak, the size dependence of the oscillator strengths, the specific influence of quantum confinement, defect-related, or Si/SiO\(_2\) interfacial states on photoluminescence; and the direct or indirect nature of the transition between discrete or continuous energy levels. The lack of information that could help answer all these open questions is mostly because most of the studies have concerned the behavior of the emission spectra, whereas only a few studies [59-62] have addressed the experimental investigations of the optical absorption processes in such a complex system.
Figure (1-16): Linear absorption of the sample in the UV–VIS range in Si/SiO$_2$ nanostructure absorption dominated by direct transitions and evidence of quantum confinement [59].

Optical properties of semiconductor quantum structures with reduced dimensions have been the subject of many experimental and theoretical studies. One of the motivations for these studies has been stimulated by the discovery of visible luminescence from porous Si. Although there is still debate on the origin of photoluminescence, there is considerable experimental and theoretical evidence for the role of quantum confinement (QC) in producing this phenomenon [63].

1.12.2 Photoluminescence (PL)

Photoluminescence in simple terms is a reverse process of absorption. The energy of the laser light should exceed the bandgap energy of the semiconductor in order not to lose information. However, the absorption spectrum of a material contains all possible transitions while photoluminescence involves emission of a particular wavelength that
corresponds to the transition. Photoluminescence occurs when an excited electron in an excited state returns to the initial state by emission of a photon whose energy gives the difference between the excited state and the initial state energies. The process can be direct or indirect depending on the gap energy [43].

Efficient emission of visible light has been observed from silicon nanostructure [64]. Theoretical calculations with experimental absorption and photoluminescence data is fair and that is due to the strong correlation of the optical gap with the nanoparticle size. While this finding provides an important piece of evidence for QC models, a complete microscopic understanding of the size dependence of optical excitations in Si nanocrystals and porous Si is yet to be achieved [63].

The quantum confinement model has been widely used by Suemoto et al. [65] and modified by Yorikawa et al. [66] to study the nanocrystallite size distributions in porous silicon from its PL spectra. According to the QC model, the emission wavelength and intensity depend on the nanocrystal diameter, size distribution and concentration. This model can explain the general tendency of most of the experimental results such as the blue-shift of the luminescence spectrum with a decrease of the Si-nc size. It is based on the fact that each nanoparticle in a porous silicon specimen contributes a characteristic sharp PL spectrum, where the total PL intensity $S(E)$ from an assembly of particles including size distribution is given by:

$$S(E) = c \alpha \left( E_{exc} - E \right) D(R_\alpha) \left( \frac{1}{n} \right) \frac{R_g}{E - E_g}$$  \hspace{1cm} (1-23)
where \( E_g^* \) is the gap energy of bulk silicon, \( R_E \) is the crystallite radius defined by

\[
R_E = \left( \frac{\gamma}{E - E_g^*} \right)^{\frac{1}{n}} \tag{1-24}
\]

where \( n = 2 \) for two-dimensional quantum confinement (i.e. wire-like structure). The coupling constant \( \gamma \) is in eV (Å)\(^2\), which gives \( E_g^* = 1.17 \) eV.

The \( c \) is a constant, which includes the intensity of the light source at the excitation energy \( E_{exc} \) and \( \alpha(E_{exc} - E) \) is the absorption coefficient. The function \( \alpha(E) \) can be reduced to a simple form such as \( \alpha(E) = (a_1 + a_2E^2) \), where \( a_1 \) and \( a_2 \) are temperature-dependent constants [65].

In order to explain the effect the size distribution of nanoparticles in P-Si, we need to use the Gaussian function in equation (1-24), this function is:

\[
D(R) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ \frac{(R - \bar{R})^2}{2\sigma^2} \right] \tag{1-25}
\]

where \( R \) is the particle radius and the particle diameter \( L = 2R \), \( \sigma \) is the standard deviation. The Gaussian function allows very small nanoparticles with \( R \to 0 \) to contribute in the photoluminescence. The quantum confinement model proposed by Suemoto et al. [65] represents a physical and not mathematical model. In addition, this model gives significant information on the nanoparticles sizes and their distribution and the most important thing is the indication about the Si nanoparticles energy gaps.

The size-quantization effect in semiconductor nanoparticles stimulated research on nanostructured materials and generates great interest in the scientific community and thereby, this offers tremendous opportunities in the field of physics, chemistry, materials science, and related interdisciplinary
areas because of the properties exhibited by them and the challenging problems thrown up for providing theoretical concepts in physics associated with it. Optical properties of nanocrystals are markedly related to their size and surface chemistry and drastically differed from those of bulk materials [67].

Although these nanostructured materials have been the subject of numerous studies, the mechanism of visible luminescence has not yet been completely established. Models involving quantum confinement of excitons and interface electronic states have been proposed in attempts to explain this phenomenon. Quantum confinement should in principle lead to size-dependent luminescence spectra, if this is the dominant mechanism for photocarrier recombination. Experimental confirmation of this mechanism requires that measurements be made either on single nanocrystals or ensembles having carefully controlled sizes. Although size classification of silicon nanocrystals has been achieved to a certain extent by size-selective chemical precipitation, as also demonstrated for II–VI semiconductor crystallites, most of the studies to date have involved samples with broad size distributions containing large chains of nanostructures, thereby complicating the interpretation of the luminescence behavior. These nanocrystals can potentially be used in optical experiments and help clarify the luminescence mechanism [68].

1.12.1 Morphological Properties

The formation of small crystalline grains with low-dimensional quantum effect properties is expected [69]. Characterization of silicon nanoparticles structure had been conducted using scanning electron (SEM)
and atomic force microscopy (AFM) in order to gain an understanding of their formation mechanisms.

Nanosecond pulsed laser irradiation can induce surface modifications of materials in the micro- and nano-scale. The metric of the modification is a function of melting time and the amount of ablated material, which are a function of the laser fluence and wavelength [70].

![SEM micrographs of the Si films deposited with a hemicylindrical configuration at 0° and 45° with respect to the target normal for fluences of 3.0 and 4.0 J/cm²][71].

The size of the surfaces and the measurement speed can limit use of techniques such as AFM. The AFM is better technique for research and development studies. Surface roughness plays a part also in the research and development of soft materials [72].
Chapter One: Theoretical Background

Figure (1-18): AFM images of Si NPs on the area of the substrate where the debris appears as isolated particles formed by femtosecond laser ablation [73].

Determination of the heights, locations, and curvatures of summits on contact surfaces is necessary to model contact and friction. While this would seem to be a straightforward task, the multiscale roughness properties of real surfaces make the concept of a “summit” ambiguous and imprecise [74].

The most challenging task in preparing Si-nanoparticles is to succeed in controlling the particle size and morphology as well as the surface properties [75].

1.13 Applications of Silicon Nanostructure

Silicon is the dominant semiconductors in the device technology today. There are some reasons why Si is the semiconductor material of choice. Among these, the two fundamental reasons are the following. The first is the raw material that can be used to produce Si-wafer (sand) is readily available. The second reason is that it possesses good mechanical and thermal properties. The bulk of the Si-wafer is, for example, provides good mechanical support
for the fabricated electronic devices, which reside in the region near the wafers surface [25].

The past decades have witnessed a breathtaking progress in semiconductor device fabrication techniques, with a relentless trend towards miniaturization [76].

Silicon nanoparticles are important nanomaterials both for applications in optoelectronics [77], microelectronics and biomedical areas [78]. Si nanoparticles/nanocrystals with visible light emission have been prepared by a number of techniques, such as electrochemical etch, laser pyrolysis, ion sputtering, ion implantation, chemical vapor deposition, spark-processing technique and pulsed laser deposition (PLD).

Applications of nanostructures and nanomaterials are based on (i) the peculiar physical properties of nanosized materials, like gold nanoparticles used as inorganic dye to introduce colors into glass and as low temperature catalyst, (ii) the huge surface area, such as mesoporous produced by photoelectrochemical cells, and nanoparticles for various sensors, and (iii) the small size that offers extra possibilities for manipulation and room for accommodating multiple functionalities. For many applications, new materials and new properties are introduced. For example, various organic molecules are incorporated into electronic devices, such as sensors [63].

Silicon nanotechnology is up coming and the promising one. The Nanosilicon (crystalline as well as amorphous) exhibits intense luminescence. Therefore, several applications have been predicted for nanocrystals, ranging from simple dyes to magnetic-resonance-imaging contrast agents, components
of electronic circuits, and magnetic media, in gradients in catalysts and sensors and so on. All the above applications seek to exploit the tunability provided by the size dependent properties of the nanocrystals [25].

1.14 Applications of Silicon Nanoparticles

Silicon nanotechnology is up coming and the promising one. The Nano-silicon (crystalline as well as amorphous) does luminescence. It is this photoluminescence (PL) properties of nanocrystalline silicon (nc-Si) is of major debates in recent days [25].

The tunability of the energy gap can be used to make light sources and detectors for specific use. In addition, when discrete energy levels are formed with decreasing particle size [3].

Amorphous silicon has been the subject of intense experimental and theoretical interest in recent years, not only as an interesting material for a variety of useful optical and electronic devices, but also as an excellent system for the study of amorphous materials. These investigations have been responsible for significant contributions to the development of commercially important electronic device applications, such as flat panel displays, and photoelectric devices, such as sensor arrays and solar cells [4].
This chapter concentrates on the description of the PLD technique for fabricating Silicon nanoparticles films and then discusses which diagnostic tools to examine these parameters. This leads to a natural demarcation of the analytical tools, into those for examining the spectroscopy, the structural and surface morphology properties of the deposited films.

2.1 Laser Ablation

The principle of laser ablation is shown in figure (2.1). A pulsed laser is focused on a solid target, placed in a vacuum chamber. The laser energy focused on the target material that locally creates plasma, the so-called ablation plume. This plasma is directed and expanded perpendicularly to the target. The propagating ablated species are then collected on a substrate placed in front and at a given distance from the target. The fabrication parameters can be easily changed in a wide range.

![Figure (2-1): Pulsed laser ablation set-up](image)

The following instruments have been used in this work:
2.2 The Ablation Equipment

2.2.1 Nd:YAG Laser

A Q-switched Nd:YAG laser emits light at a wavelength of 1064 nm, in the near infrared and at 532 nm in the visible region of the electromagnetic spectrum with a pulse duration of 10ns and frequency 1 Hz was used as good quality of laser beam $M^2 = \frac{D^* \Theta_0 \pi}{4\lambda}$, $D^*$: output diameter for a flat output window, $\Theta_0$: divergence angle for the beam expansion at infinity, $\lambda$: laser wavelength, for TEM$_{00}$ ideal $M^2=1$ where it has a uniform distribution of intensity across the beam cross section. This is important because deviations from homogeneity (so called hot spots) may result in droplet formation, as well as deviations in stoichiometry of the deposit.

2.2.2 The Focusing

A Nd-YAG laser was focused by spherical lens and then focused onto the solid target surface by using quartz lenses mounted inside the vacuum chamber. This is necessary to exceed the threshold power density for the ablation as the beam hits the target surface.

2.3 Deposition Chamber

Since the PLA system does not necessarily require ultra-high vacuum, the geometry of the chamber can be designed quite freely. When designing a chamber, at least the following aspects should be taken into account: The arrangement of the components inside the chamber should not disturb the path of the laser beam. Access to the target and to the substrate should be straightforward, since these components will be changed frequently. The target-to-substrate distance should be adjustable. A glass bell-jar of $(0.15\text{m}^3)$ has been used for the ablation process to observe the plume formation and the deposition process.
2.3.1 Target

The target was a single crystal silicon wafer of conductivity n-type, (111) orientation and resistively of $2 \times 10^{-4} \, \Omega \cdot \text{cm}$. In addition, it is recommended to resurface (grind and/or polish) the target frequently to avoid the generation of the particulates during the deposition.

The target was rotated to preclude pit formation and ensure uniform ablation of the target. The target mount was fixed at angle of 45° with the incident laser pulse.

2.3.2 Substrate

The most important features of a substrate holder are its movement relative to the target and plasma plume and, in some cases, ability to heat the substrate. Even with the simplest substrate holders, one should be able to adjust the distance between the target and the substrate. (This is usually performed by changing the position of the substrate, not the target)

The adjustment of the target-to-substrate distance provides an opportunity to control the deposition rate, as well as the energy of the particles hitting the substrate. The uniformity of the coating thickness may require rotative motion of the substrate during the deposition.

The substrate used for deposition of silicon nanoparticles was borosilicate glass slides, which was cleaned in distilled water to remove the residuals and impurities from their surface and then cleaned with ethanol.
2.3.3 The Vacuum System

Most of the applications of PLA do not require ultra high vacuum (UHV). Deposition can vary on a wide range ($10^{-2} \ldots 10^{-7}$ Pa) depending on whether a reactive background gas is used or not, so there are various alternatives for the pumping systems. However, since clean and oil-free atmosphere is important for thin film deposition, vacuum pumps with the risk of oil diffusion into the chamber (e.g. diffusion pumps) are not favored.

In this work, a pressure of $2 \times 10^{-4}$ torr was used during the deposition, A PLA-system may contain two types of vacuum gauges, ionization-based gauge (pinning gauge) for the lowest pressures, a pirani gauge for the middle pressure level.

2.4 Preparation Technique

Silicon nanoparticles films were deposited on glass substrate under various preparation parameters such as number of pulses, laser energy, target-to-substrate distance and laser wavelength.

Three of these parameters were fixed and one of them was mode variable to study its effect on the nanostructured films.
Figure (2-2): Sketch of the experimental work show of preparation parameters and study characterization
2.5 Characterization Measurements

2.5.1 The Film Thickness

A silicon nanostructured film thickness has been measured by an interference fringes method \[79\]. A He:Ne laser (\(\lambda = 632.8\) nm) was used as a light source to measure the thickness. The laser beam is focused on the sample using quartz lens of 5 cm focal length. The sample was mounted at suitable angle with the incident laser beam. The interference of the laser beam reflection from thin film surface and substrate bottom were observed on a dark background. The film thickness was estimated by using the formula:

\[
t = \frac{\Delta x \cdot \lambda}{2x}
\]  

(2-1)

Where \(x\) is the fringe width, \(\Delta x\) is the fringe spacing and \(\lambda\) is the wavelength.

2.5.2 Transmittance and Reflectance Measurements

The optical properties of the thin films were studied by optical transmittance and reflectance spectroscopy. The spectra were obtained at room temperature. A Cary 5000 UV-VIS-NIR (175-3300nm) spectrophotometer was employed to study the optical Transmittance (\(T\)) and Reflectance (\(R\)) for Si-NPs/glass thin films prepared in different conditions for wavelength interval between 280-800 nm.
Analysis of optical transmission ($T$) and reflectance ($R$) spectra is one of the most productive tools for the understanding the band structure and bandgap ($E_g$) of both crystalline and amorphous non-metallic materials [80]. The absorption coefficient was calculated from Beer-Lambert law, ($\alpha$) which is expressed in terms of the intensity of the incident light ($I_o$) and the intensity of transmitted light ($I$) after passing through a thickness ($t$) [81] as

$$I = I_o e^{-\alpha t} \quad (2-2)$$

Absorbance ($A$), is defined as the logarithm (base 10) of the reciprocal of the transmittance:

$$A = -\log \frac{1}{T} = -\log_{10} \left( \frac{I}{I_o} \right) \quad (2-3)$$

So,

$$\alpha = 2.303 \cdot \frac{A}{t} \quad (2-4)$$
This coefficient is slightly affected by the change of structure at lower energy values. This behavior is probably due to the crystallization process occurring in the films [82].

Figure (2-4) represents the spectral variation of the reflectivity ($R$) of the reference circular mirror used in the reflectance measurement of the films deposited on glass substrates.

\[
R_{\text{calculated}} = \frac{R_{\text{measure}} \times \frac{R_{\text{reference}}}{\text{Baseline}}}{100} \quad \text{(Privy comment)} \quad (2-5)
\]

![Figure (2-4): Typical Reflectance vs. Wavelength of the Enhanced Aluminum Mirror](image-url)
2.5.3 Calculation of Optical Constants (Cauchy's Model)

The most important elements that can be calculated by the Java optics program are the Transmittance \( T(\lambda) \) and Reflectance \( R(\lambda) \) spectra of the sample. To calculate these values from the refractive index \( n \), extinction coefficient \( k \) and the thickness of the thin film \( t \), it is necessary to consider the cauchy's model.

The window of “Transmission and Reflection” allows changing the thickness of the layer (\( t \)), the wavelength of the incident light (\( \lambda \)), and the angle of incidence (\( \theta \)). Furthermore, the values of the refractive index (\( n \)) and extinction coefficient (\( k \)) can be changed by means of the buttons “Change \( n \)” and “Change \( k \)”. These open two windows with the names “Refractive index parameters” and “Extinction coefficient parameters” respectively. These parameters correspond to a mathematical model for the refractive index and the extinction coefficient that follows the expression [83]:

\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}; \quad (2-6)
\]

\[
k(\lambda) = k, \exp\left(D_0 / \lambda\right) \quad (2-7)
\]

These windows allow changing the values of \( A, B, C, k_0 \) and \( D_0 \) and show a plot of these indices against the wavelength.

2.5.4 Photoluminescence Measurements

Photoluminescence (PL) spectroscopy is an important tool to study the excited electronic states in solids. PL intensity is determined by the population density of excited states and the quantum yield. Therefore, PL
may provide an insight into relaxation dynamics of excited states. Measuring PL from distinctly populated excited electronic states enables, for instance, to examine effects from electron-electron interactions on PL spectra.

The photoluminescence setup equipped with various excitation sources (Ar Ion laser-UV extended and 1000 W monochromatized-Xe lamp); a 0.5 m single and a 0.75 m (optical path) double spectrometers; a cooled GaAs and InGaAs photomultipliers for photon-counting, a cooled Ge avalanche photodiode with lock-in and chopper, and an optical multichannel array (EG&G OMA); A computer controlled VSL system was available for routine measurements of optical gain. Computers were employed to control all the measurements. Low laser power density of 0.2 W/cm² was used for the excitation to avoid excessive heating and its effect on photoluminescence.

Figure (2-5): (a) Schematic diagram of PL system (b) The experimental Set-up of PL, University of Trento - Italy.
2.5.5 Raman Spectroscopy Measurements

Raman scattering measurements in fully backscattering geometry were conducted at RT on samples brought in air, using a microprobe setup (Horiba-Jobin-Yvon, Labram HR), consisting of a He–Ne laser (excitation wavelength: 632.8 nm), a narrow-band notch filter (Holographic super-notch filter of the Kaiser Optical Systems Inc.) a 80 cm focal length spectrograph, mounting a 1800 grooves/mm grating, and a charge coupled device detector cooled by liquid nitrogen. The laser beam was focused onto the sample surface, with a spot size of about 2 μm (focal spot area of about 3 μm²), by means of a 100× objective with numerical aperture NA= 0.9. At the occurrence, neutral filters of different optical densities were used to avoid unwanted effects due to laser heating. The spectral resolution was about 2 cm⁻¹/pixel.

By analysing the change in the photon energies, it is possible to get information about the characteristic vibrational energies of the specimen. Since the vibration states are specific for chemical bonds, the atoms and molecules in the specimen surface can be determined. In characterization of PLD coatings, the applications of Raman spectroscopy are similar to X-ray Photoelectron Spectroscopy (XPS) [53].

Figure (2-6): Schematic diagram of the Raman spectroscopy system.
2.5.6 X-Ray Diffraction (XRD)

XRD is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of polycrystals, defects, stresses, etc. In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 Å, is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law [84]:

\[ n\lambda = 2d \sin \theta \]  

(2-8)

Where \( d \) is the spacing between atomic planes in the crystalline phase and \( \lambda \) is the X-ray wavelength. The intensity of the diffracted X-rays is measured as a function of the diffraction angle \( 2\theta \) and the specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties. XRD is nondestructive and does not require elaborate sample preparation, which partly explains the wide usage of XRD method in materials characterization.

The crystallite size, \( D \), can be estimated from the peak width with the Scherrer's formula [85]:

\[ D = \frac{K\lambda}{B \cos \theta_B} \]  

(2-9)

Where \( \lambda \) is the X-ray wavelength, \( B \) is the full width at half maximum (FWHM) of a diffraction peak, \( \theta_B \) is the diffraction angle, and \( K \) is the
Scherrer’s constant of the order of unity for usual crystal. However, one should be alerted to the fact that nanoparticles often form twinned structures; therefore, Scherrer’s formula may produce results different from the true particle sizes.

The X-ray diffraction (XRD) patterns were collected using a Rigaku III/D Max powder diffractmeter with Bragg-Brentano goniometry. The system is operated with copper radiation (Cu $K_a$ radiation at $\lambda=0.15418$ nm wavelength), monochromatized by a flat graphite crystal analyzer in the diffracted beam. The instrument is equipped with 1° divergence and scattering slits, 2° primary and secondary seller slits and 0.15 nm receiving slit. The XRD patterns of samples were recorded in the range $2\theta=10-70^\circ$ using a step size of 0.1° and a counting time of 5 sec/step. The diffractometer was operated at 20 kV and 30 mA.

2.5.7 Microscopy:

1. Atomic Force Microscopy (AFM)

AFM has evolved as a promising device to explore the mineral surface, visualize the sorption of organic substances and determine morphology, measure size and thickness of particles.

The morphology of the Si nanoparticles film is very sensitive to the deposition parameters, such as the number of laser pulses, laser energy and target-to-substrate distance.

A Solver P-47H (Digital Instruments Nanoscope NT-MDT SOLVER P47H-PRO) AFM is equipped with SFC090SEMI head that is able to operate in air in contact mode, in non-contact mode and in intermittent
contact mode. The head is equipped with a 90×90×5 mm piezoelectric-tube scanner, which moves the probe in the (x,y) plane and in z direction respect to the sample. The probe, coupled to the scanner, is essentially a sharp tip located at the free end of a flexible cantilever. The cantilever is fixed on a solid substrate inserted in a probe holder situated on the scanner.

The AFM images have been analysed using available software namely Image analysis (2). This software packages offer a wide variety of functions related to AFM image analysis including cross-section profile analysis, roughness analysis, grain/pore analysis, 3D visualization and histogram analysis, etc. Line profiles were employed to estimate size and height of nanoparticles. Nanoparticle density has been calculated by counting particles in the window using the image processor.

The head is also provided of a tip-to-sample manual approach system for stand-alone operation as shown in Figure (2-7a).

An optical viewing system is placed side by side to the AFM head in order to line up a laser spot on the cantilever and to place the probe on the sample. It is composed of a video-microscope with manual zoom and CCD, and a monitor.

The picture of the AFM is shown in Figure (2-7b) below.
Chapter Two: Experimental Details

2. Scanning Electron Microscopy (SEM)

SEM is one of the most widely used techniques in characterization of nanomaterials and nanostructures. The resolution of the SEM approaches a few nanometers, and the instrument can operate at magnifications that are

Figure (2-7): (a) The schematic diagram of AFM (b) A photo of AFM microscope, University of Trento - Italy.
easily adjusted from ~ 10 to over 300,000. Not only does the SEM produce topographical information as optical microscopes do, it also provides the chemical composition information near the surface [84].

Electron microscopy is a method of choice to investigate particles size, shape and structure also agglomerates. In SEM experiments, electrons emitted from filament are reflected by the sample and images are formed using either secondary electrons or backscattered electrons. However, in the case of SEM, a field emission microscopy (FE-SEM) is necessary to investigate the nanometric scale (electrons are emitted from a field-emission gun) FE microscopes could reach resolutions of the order (1 nm) using a cold cathode.

The JSM-7001F, a new thermal field-emission analytical scanning electron microscope (SEM) from electron optical product maker JEOL USA, acquires high-resolution micrographs at up to 1,000,000X magnification for applications ranging from semiconductors, metals, minerals, materials and ceramics to nonconductive biological samples.

The JSM-7001F features a unique in-lens field emission gun that delivers more than 200 mA of beam current to the sample. An extremely small probe diameter at low kV and high current is optimal for characterization of nanostructures with a resolution of 1.2 nm at 30 kV. According to JEOL, the JSM-7001F is ideal for low accelerating voltage x-ray spectroscopy and crystallography at and below the 100 nm scale. The large specimen chamber is designed for samples up to 200 mm in diameter.
Figure (2-8): (a) Schematic diagram of a scanning electron microscope (b) A photo of FESEM JEOL-7001 F microscope, University of Trento-Italy.
Chapter three investigates effects of the experimental parameters on the optical and electronical properties of the silicon nanostructured thin films prepared by laser ablation and demonstrates results of the transmittance ($T$), reflectance ($R$), Refractive index ($n$) and Extinction coefficient ($k$), optical bandgaps ($E_g$), Raman spectroscopy and photoluminescence ($PL$) for both the UV-visible electromagnetic spectrum.

Moreover, this chapter examines the effect of the experimental parameters on the structural properties by X-ray diffraction (XRD) and the surface morphology using the atomic force microscopy (AFM) and scanning electron microscopy (SEM). These observations suggest that several nanometer size Si particles were prepared by the PLA using two Nd:YAG laser wavelengths the (1064 nm) and the second harmonic (532 nm).

3.1 The Optical Properties

The optical properties were investigated for samples prepared by laser ablation. These properties include:

3.1.1 The Optical Transmittance

UV-visible spectrophotometer measurements of Si nanoparticles thin films were curved out for the samples deposited by different parameters. Figure (3-1) shows the transmittance ($T$) versus the wavelength of these films deposited on glass substrates. The average visible transmittance of these films increases with a variation of different parameters. This is mainly due to the
decrease in the film thickness, which leads to lesser scattering and absorption of photons.

Studying the optical transmittance of the prepared film is of great interest due to its valuable scientific meaning. The optical transmittance spectra depend on the crystalline structure of the prepared films and on the surface morphology. Figure (3-1) shows the effect of various preparation parameters on the transmittance spectra. The transmittance of the deposited film was examined in the ultraviolet and visible ranges. It was found that all films prepared by this technique have high transmittance at longer wavelengths.

1. Effect of Number of Laser Pulses

Figure (3-1a) explains that the transmittance spectrum decreases exponentially with increasing the number of pulses for a specific wavelength. This could be attributed to the increase in the amount of the ejected particles reaching the substrate surface. This large amount of particles will increase the film thickness and subsequently decrease the transmittance. The sharp increase in the transmission spectrum varies from one film to another; this may be explained by the variation in the particle size distribution for each sample.

2. Effect of Laser Energy

Figure (3-1b) shows the optical transmittance of the silicon nanoparticles films prepared under different laser energies. It is obvious from the figure that for a certain wavelength, the transmittance decreases with increasing laser energy of the incident laser pulse. It is clear that when the
incident laser energy increases, the amount of the absorbed energy in the target increases, which leads to an increase in the ejected particles toward the substrate. These ejected particles have higher kinetic energy when higher laser energy is absorbed and ultimately increase the particles density deposited on the substrate.

3. Effect of Target-to-Substrate Distance

Figure (3-1c) describes the behavior of the optical transmittance under different target-to-substrate distances. The spectra show an increase in the transmittance when the target-to-substrate distance increased from (0.4-0.8 cm). This is probably related to the fact that the decreasing in the number of particles reaching the substrate. Only the smaller size particles that have high kinetic energy could arrive at long distance (0.8 cm), while large particles will deviate away from the substrate.
Chapter Three: Results and Discussion

4. Effect of Laser Wavelength

Figure (3-2) shows the optical transmittance of the silicon nanoparticles films prepared under different preparation parameters such as number of pulses, laser energy and target-to-substrate distances using the second harmonic of Nd:YAG laser wavelength of 532 nm. It was found that the transmittance has the same trend for Nd:YAG laser beam of 1064 nm.
The transmittance of the second harmonic wavelength at 532 nm is higher than that at 1064 nm due to the amount of the absorbed energy by the target. This leads to a decrease in the ejected particles toward the substrate. These ejected particles have higher energy density when using the beam second harmonic wavelength which when absorbed increases the particles density deposited on the substrate as compared to the 1064 nm Nd:YAG laser.

Figure (3-2): Effect of the laser wavelength on transmission spectra for different preparation parameters as a function of (a) Number of pulses (b) Laser energy (b) target-to-substrate distance
3.1.2 The Optical Reflectance

A study was conducted in the present work to assess the surface reflectance as a function of the number of pulses, laser energy, target-to-substrate and laser wavelength, Figure (3-3) shows the surface of several silicon thin films nanoparticles for pulsed laser deposition with different parameters.

The reflectance is measured in the range of (400-700 nm). It is observed that the reflectance minimum tends to shift towards longer wavelengths.

The typical optical reflection spectra of the Si thin films nanostructures are shown in Figure (3-3). It is well known from the theory of optical transitions in semiconductors; a peak in the reflectance spectra is appeared near a band edge [86]. The optical characteristics of the nanostructured Si thin films gradually change in the visible spectral range. In addition, the intensity of this band increases with the decrease of the number of laser pulses and incident laser energy and decreases with target-to-substrate distances.

The incident photons of this wavelength were converted to surface plasmons because of interaction with the free electron distribution of silicon nanoparticles surface, leaving a gap in the reflected light intensity. The much weaker band at longer, around (630 nm) wavelength, Figure (3-3), could be assigned to the contribution of larger aggregates, composed from Si nanoparticles.
Figure (3-3): Reflectance spectra for different preparation parameters as a function of (a) Number of pulses (b) Laser energy (c) target-to-substrate \((d_{ts})\) \([\lambda_{\text{Laser}}= 1064 \text{ nm}]\)
Effect of Laser Wavelength

The reflectance variations of the background signal are clear indications that the ablation depends on the laser wavelength as shown in Figure (3-4), which governs the penetration depth of the laser beam, the temperature evolution, and the affected target volume.

![Figure (3-4): Effect of laser wavelength on reflectance spectra for different preparation parameters as a function of (a) Number of pulses (b) Laser energy (c) target-to-substrate distance]
3.1.3 Refractive index \((n)\) and Extinction coefficient \((k)\) 

The refractive index \((n\) and \(k\)) of a film can be determined from the reflectance or transmittance of a thin film measured data. The amorphous Si nanoparticles thin films were deposited on silica substrates to a thickness of several nm.

A mathematical model can be used for the fitting of the measured data. One of them is the Cauchy model, useful the absorption band. Cauchy's equation is an empirical relationship between the refractive index \((n)\) and wavelength of light \((\lambda)\) [87] for a particular transparent material.

The refractive index \((n)\) and extinction coefficient \((k)\) of the Si nanoparticles thin films of the samples prepared under different parameters as a function of Number of pulses, Laser energy and Target-to-substrate distances are presented in Figure (3-5).

Figure (3-5) reveals that all the films are transparent in the spectral region of \((400-800 \text{ nm})\) the refractive index \((n\)-values) and the extinction coefficient \((k\)-values) are increasing in the VIS region (shorter wavelengths).

The extinction coefficient is calculated using caushy's equation (chapter two).
Figure (3-5): Optical constants refractive index \((n)\) and extinction coefficient \((k)\) for different preparation parameters as a function of (a) Number of pulses (b) Laser energy (c) target-to-substrate \((d_{ts})\) \([\lambda_{Laser} = 1064 \text{ nm}]\).
Effect of Laser Wavelength

Figure (3-6) depicts effect of laser wavelength on spectra of the refractive index, $n$. The $n$ values result from films prepared in PLA with different laser wavelengths. The refractive index in of films prepared by 1064 nm is higher than films prepared by laser wavelength 532 nm for silicon nanoparticles.

![Figure (3-6): Effect of laser wavelength on refractive index ($n$) for silicon nanoparticles thin films](image)

3.1.4 Optical Bandgap

To understand the optical and electrical properties of the prepared films, it is very necessary to study and estimate the mean value of the energy bandgap. This value depends on the films structure, the arrangement and distribution of atoms in the crystal lattice. To determine the value of bandgap ($E_g$), a graph of $(\alpha)^{1/\eta}$ vs. $hv$ is plotted for different preparation conditions as
can be seen in figures (3-7 to 3-10), where the optical bandgap \( (E_g) \) represents the value of intersection point between the straight line and photon energy axis. \( (E_g) \) is the bandgap of the material and the exponent \( \eta \) depends on the kind of optical transition. For crystalline semiconductors, \( \eta \) can take values 1/2, 3/2, 2 or 3 depending on whether the transitions are direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively [88-90].

However, in low dimensional silicon (silicon nanoparticles) the bandgap is almost transferred to quasi-direct [91].

In both crystalline and amorphous semiconductors, the absorption coefficient near the fundamental absorption edge is dependent on photon energy. In the high absorption region, the absorption coefficient become more general form as a function of photon energy [92,93].

1. Effect of Number of Laser Pulses

The bandgap of the silicon nanostructure films prepared under different number of laser pulses was studied as shown in Figure (3-7). It was found that the value of the bandgap decreases with increasing the shot laser pulses, because increasing the laser pulses increases the number of particles reaching the substrate surface.

This is mainly due to the higher thickness of these films (Si nanoparticles), leading to the scattering and absorption of photons.
2. Effect of Laser Energy

It was also found that the bandgap energy is extremely affected by the incident laser energy as shown in Figure (3-8). When low laser energy is incident on the target, a small number of large size silicon nanoparticles are ablated from the target and the estimated bandgap energy was (2.61 eV). Further increase in the laser energy leads to an increase in the laser power density and consequently the number of large nanoparticles and the corresponding bandgap energy. This bandgap reached (2 eV) at higher laser
energy. More probably, the observed shift in the band-edge can be attributed to the decreasing particle size according to the quantum confinement effect.

Figure (3-8): The optical bandgap of the samples prepared under different laser energies \([E=700\text{mJ}, d_{cs}=0.6 \text{ cm}, \lambda_{\text{Laser}}=1064 \text{ nm}]\)

Figure (3-9) shows the possible indirect transition, therefore a relation \((\alpha)^{1/2} \text{ vs. } (h\nu)\) was plotted. The indirect-allowed bandgap values for the films deposited at different laser energies are given in table (3-1) it is found that the bandgap decreases with increasing the laser energy due to the size reduction. For both direct and indirect transitions, \((E_g)\) increases as the confined
dimension ($t$) decreases. This probability corresponds to the micron sized ablated particles.

Figure (3-9): The optical bandgap of the samples prepared under different laser energy (Indirect allowed transition) [No. of pulses=30, $d_{rs}$=0.6 cm, $\lambda_{Laser}$=1064 nm]

Table (3-1): represents the optical bandgap values to the samples prepared at different laser energy [Indirect allowed transition].

<table>
<thead>
<tr>
<th>Laser energy (mJ)</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap $E_g$ [eV]</td>
<td>1.65</td>
<td>1.48</td>
<td>1.42</td>
<td>1.32</td>
</tr>
</tbody>
</table>
3. Effect of Target-to-Substrate Distance

The bandgap of the nanoparticles measured from the optical absorption data at different target-to-substrate distances is shown in Figure (3-10). Table (3-2) clearly indicates an increase in the bandgap from (2.35eV) to (2.72eV) when the distance increases from (0.4cm) to (0.8cm).

Figure (3-10): The optical bandgap of the samples prepared under different target-to-substrate distances [No. of pulses=20, d_{t-s}=0.6 cm, \lambda_{laser}=1064 nm]
Figure (3-10) shows the $(\alpha^2)$ values as a function of photon energy $(h\nu)$. An almost linear relation is observed. The intersecting point with the horizontal axis corresponds to the optical bandgap. The energy of the optical gap has been evaluated to be (~2.63 eV). The bandgap is blue shifted in comparison with that of the bulk crystalline silicon (1.14 eV), which suggests a bandgap widening due to the quantum confinement effect [22].

4. Effect of Laser Wavelength

The laser wavelength ($\lambda$) comes into play mainly in the effectiveness of the absorption of the laser power by the target. For most metals, the absorption coefficient ($\alpha$) decreases with decreasing wavelength ($\lambda$). Hence, the laser penetration depth in metals is larger in the (UV) range than in the infrared (IR) range. The quantum confinement effect could explain that the bandgap of materials decreases as the size of quantum structure increases, which results in a red shift in optical luminescence energy. Therefore, it could be expected that the nanocrystallite size is increased by the increase of laser wavelength. Table (3-2) gives the optical bandgap of the laser deposition thin film. It is found that at shorter laser wavelength (532 nm), the bandgap is greater than those for longer wavelengths (1064 nm). This could be attributed to the higher photon energy of (532 nm) which produces smaller nanoparticles. Similarly, with other semiconductors, the penetration depth of laser into silicon increases with the increase of wavelength in PLA. As the laser wavelength increases, there is more possibility that the larger nanocrystallite are formed on the substrate surface [10].
Table (3-2): represents the optical bandgap values to the samples prepared at different preparation parameters

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>BANDGAP (eV)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Number of pulses</td>
<td>2.63</td>
<td>2.44</td>
<td>2.27</td>
<td>2.00</td>
</tr>
<tr>
<td>Laser energy (mJ)</td>
<td>400</td>
<td>500</td>
<td>600</td>
<td>700</td>
</tr>
<tr>
<td>(\lambda_{\text{Laser}}=1064\ \text{nm})</td>
<td>2.61</td>
<td>2.25</td>
<td>2.10</td>
<td>2.00</td>
</tr>
<tr>
<td>(\lambda_{\text{Laser}}=532\ \text{nm})</td>
<td>2.73</td>
<td>2.75</td>
<td>2.44</td>
<td>2.25</td>
</tr>
<tr>
<td>Target-to-substrate (cm)</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>(\lambda_{\text{Laser}}=1064\ \text{nm})</td>
<td>2.35</td>
<td>2.30</td>
<td>2.65</td>
<td>-</td>
</tr>
<tr>
<td>(\lambda_{\text{Laser}}=532\ \text{nm})</td>
<td>2.56</td>
<td>2.18</td>
<td>2.68</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2 Film Thickness

Thickness is a crucial parameter of thin films: the optical (transmission) and electronic properties of the film are highly dependent on its thickness and thickness uniformity. Applications in optics where optical interference effects are involved require the film thickness to be controlled within a small fraction of the wavelength of visible light. Therefore, for PLA, where the forwardly directed plume distribution is the most striking feature, it is essential to study the thickness profiles of the grown films.

Figure (3-11) illustrates the effect of different preparation parameters on the film thickness. A film thickness as a function of the number of pulses is shown in Figure (3-11a). Obviously, the thickness increases with increasing the number of incident pulses. Then dramatic increase in the film thickness will take place when increasing the number of pulses between (10-30). This
could be attributed to the decrease in the laser power density due to the
removal of the ejected material and change in the target surface (defocusing of
the laser beam) [94].

Figure (3-11b), shows the effect of incident laser energy on the
deposited film thickness. The results show an exponential increase of the
thickness with increasing the laser energy. The increasing of the laser energy
leads to an increase in the target absorption. Therefore, large amount of
particles will have high mean kinetic energy leading to an increase in the
number of particles reaching the substrate, which increases the film thickness.

Film thickness of the ablated plasma demonstrates that the laser
wavelength figure (3-11b), defines the nature of the ablation process. Infrared
light ($\lambda_{\text{Laser}}=1064$ nm) penetrates deep into the bulk of the material and causes
thermal ablation in a larger thickness, On the other hand, visible light ($\lambda_{\text{Laser}}=532$ nm) is highly absorbed by the target, affecting mostly the surface
layer and is a non-thermal process that causes high photo-fragmentation of the
ablated species.

Effect of the target-to-substrate distance has also been studied. Figure
(3-11c), represents the relation between film's thickness and distance between
the target and the substrate. It is clear that the deposited film thickness is
inversely proportional to the target-to-substrate distance. This is due to two
reasons, first, is the free path to the particle, where the probability of arriving
the particle to the substrate increases with increasing the mean free path of the
ablated particles. Therefore, only particles with high kinetic energy can reach
the substrate surface at long distance. Second, is the amount the molten
material ejected from the target, which is much higher at short distance (0.4
cm) which makes the film thicker (210 nm). This result is consistent with our observations for the effect of the distance in the surface morphology study (comes later).

Figure (3-11): The thickness to the samples prepared under different preparation parameters as a function of (a) Number of pulses (b) Laser energy (c) $d_{ts}$
3.3 Photoluminescence measurements

This section focuses on the PL results of the Si nanoparticles produced by laser ablation. Effects of different parameters on the photoluminescence spectrum of nanoparticles size and distribution: laser energy, laser wavelength and the target-to-substrate distance have been extensively investigated.

The study of silicon nanostructures is a very active field of research due to the strong room-temperature photoluminescence (PL) and the observation of quantum size effects. A bright red PL was first observed from porous Si [64].

Porous silicon and nanocrystalline silicon films, exhibiting PL in the visible range, belong to low-dimension structures [44,95].

Photoluminescence spectra measured at room temperature of the nanocrystalline Si thin film deposited on glass surface of samples are shown in Figures (3-12 to 3-15) using luminescence spectrometer. All plots contain two peaks: blue and red PL emissions. The excitation wavelength was 365 nm from an argon-ion laser with a power density of 40 mW/cm².

The appearance of broad peaks centered at red region is attributed to the presence of silicon vacancies in the lattice. This emission results from the recombination of photo generated charge carriers in shallow traps. The other peak centered at blue region is due to the band-to-band transition of nanocrystalline Si. The absorption edge of UV-VIS spectra appeared at the same position, which support the PL result.
The PL spectra obtained from the experimental data have been fitted to spectra calculated by the quantum confinement model of electrons within dot particle structure as shown in Figure (3-12). The theoretical calculations are shown as continuous curves. As the number of pulses is increased from 20 to 30 pulses, the mean particles size increases from 24.8 to 25 Å as given in table (3-3).

Figure (3-12): The experimentally observed PL spectra of ablated Si-nc samples for different number of pulses (discrete points) left column. The corresponding Gaussian distributions are given in the right column. \( E=700\text{mJ}, d_{\text{t-s}}=0.6 \text{ cm}, \lambda_{\text{Laser}}=1064 \text{ nm} \)

<table>
<thead>
<tr>
<th>Number of pulses</th>
<th>( L_{o1} ) (Å)</th>
<th>( L_{o2} ) (Å)</th>
<th>( \sigma_1 ) (Å)</th>
<th>( \sigma_2 ) (Å)</th>
<th>PL(_1) peak position (eV)</th>
<th>PL(_2) peak position (eV)</th>
<th>FWHM(_1) (eV)</th>
<th>FWHM(_2) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>24.8</td>
<td>18.72</td>
<td>1.3</td>
<td>0.44</td>
<td>1.7^{\text{#}}</td>
<td>2.318</td>
<td>0.31</td>
<td>0.27</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>18.76</td>
<td>1</td>
<td>0.4</td>
<td>1.78</td>
<td>2.311</td>
<td>0.32</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table (3-3): The calculated nanocrystallite sizes of Si-nc samples prepared with different number of pulses and the experimentally observed FWHM as well as PL peak position.
1. Effect of Laser Energy

Si nanoparticles show an intense light emission at room temperature in the visible region. This light emission is a result of the radiative recombination of electron-hole pairs confined within the nanocrystals. Figure (3-13) shows PL spectra from the Si nanoparticles films ablated by Nd:YAG laser system with different laser energy. The calculated PL spectra are shown by continuous curves in Figure (3-13), while the experimental data are plotted as discrete points. The Gaussian distributions for the nanocrystallite size $D(R)$ used for fitting in Eq. (1-25) are given in the right column of Figure (3-15), where $D(L) = D(2R)$. The crystallite sizes distribution parameters used in the fitting procedure are given in Table (3-4).

For the sample prepared with 500 mJ laser energy, the PL band appears with the first peak position. It was found that the particle size is about 23.6 Å and the standard deviation is 1.1 Å at the second peak position it was found that the particle size is 16.2 Å, and the standard deviation is 1 Å as shown in Figure (3-13). With increasing the incident laser energy up to 700 mJ, the nanoparticle size increased at the first peak position to 25 Å with a standard deviation of 1 Å and at the second peak position to 18.76 Å, with a standard deviation of 0.4 Å.

This shift of the PL spectrum is a result of increasing the vaporized materials with laser energy, because this material almost has smaller sizes. Since the excitation source has a photon energy larger than the bandgap of the synthesized nanoparticles, therefore, efficient absorption process will take place from Si-nanoparticles leading to the generation of a wide range of particle sizes within the Si deposited film. The quantum confinement effect
could explain the decrease in the energy bandgap associated with the increasing in the laser energy as attributed to the increase of particles sizes.

It should also be mentioned here that the photoluminescence intensity becomes higher for high laser energy and that is due to the high number of small nanoparticles contributing to the emission.

We fitted the PL spectra of Si nanoparticles in the samples deposited under various laser energy by varying the size $R_0$ and the size distribution $\sigma$. Table (3-4) reports the size of Si nanoparticles calculated from fits of PL spectra.

These spectra should reasonably show the blue shift of PL peak as increasing the laser energy. This case emerged in our morphological study (AFM) for different laser energies (will be discussed in section 3.7). The reason for this blue shift is so as the ejected materials were supplied with more kinetic energy during deposition process by higher laser energy density [10]. Our results show a red shift of the PL spectra with increasing the laser energy. The reason behind this is attributed to the large number of pulses we have used since low number of pulses exhibit a very weak PL intensity that could not be distinguished. Therefore, one could expect that for small number of laser pulses a blue shift of the PL spectra could be observed with increasing the laser energy.

The NPs exhibited a strong red luminescence of the visible spectrum. The PL emission measured at room temperature consists of a broadband spectrum in the approximate range of 400 nm to more than 800 nm (800 nm
Chapter Three: Results and Discussion

being the upper limit of our spectroscopic system). The maximum intensity emission is centered at ~ 690 nm (~ 1.8 eV).

Figure (3-13): The experimentally observed PL spectra of ablated Si-nc samples for different laser energies (discrete points) left column. The corresponding Gaussian distributions are given in the right column. [No. of pulses=30, d_{ps}=0.6 cm, λ_{Laser}=1064 nm]

Table (3-4): The calculated nanoparticles sizes of Si-nc samples prepared with different laser energy and the experimentally observed FWHM as well as PL peak position.

<table>
<thead>
<tr>
<th>Laser Energy (mJ)</th>
<th>L_{o1} (Å)</th>
<th>L_{o2} (Å)</th>
<th>σ_1 (Å)</th>
<th>σ_2 (Å)</th>
<th>PL_{1} peak position (eV)</th>
<th>PL_{2} peak position (eV)</th>
<th>FWHM_{1} (eV)</th>
<th>FWHM_{2} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>23.6</td>
<td>16.2</td>
<td>1.1</td>
<td>1</td>
<td>1.85</td>
<td>2.695</td>
<td>0.29</td>
<td>0.95</td>
</tr>
<tr>
<td>600</td>
<td>24.6</td>
<td>16</td>
<td>1</td>
<td>0.6</td>
<td>1.805</td>
<td>2.741</td>
<td>0.25</td>
<td>0.58</td>
</tr>
<tr>
<td>700</td>
<td>25</td>
<td>18.76</td>
<td>1</td>
<td>0.4</td>
<td>1.78</td>
<td>2.311</td>
<td>0.32</td>
<td>0.24</td>
</tr>
</tbody>
</table>

2. Effect of Target-to-Substrate Distances

Figure (3-14) shows PL spectra obtained from Si-nanoparticles samples ablated at different target-to-substrate distances varied from 0.4 to 0.8 cm. At
a distance of 0.4 cm, the PL band appears at first peak position is 1.78 eV and the second peak position is 2.63 eV. When the distance between target and substrate is increased from 0.4 to 0.6 cm, the first PL peak position shifts from 1.78 to 1.85 eV and the second peak position shifts from 2.63 to 2.695 eV. When the distance is further increased to 0.8 cm, the PL peak position energy decreases and the first PL peak position shifts from 1.78 to 1.814 eV while the second peak position shifts from 2.311 to 2.555 eV. Both the PL intensity as well as the diameter of the particle decreased as given in table (3-5).

These observations clearly indicate an optimum distance between target and substrate for obtaining maximum PL yield from Si-nanoparticle samples or smaller nanoparticle sizes. The photoluminescence of the nanoparticles in this study indicates that the minimum size is obtained at distance (0.8 cm) while number of the contributing nanoparticle is optimum at smaller distances.

**Table (3-5):** The calculated nanocrystallite sizes of Si-nc samples prepared with different target-substrate distances and the experimentally observed FWHM as well as PL peak position.

<table>
<thead>
<tr>
<th>(d_{ts}) (mm)</th>
<th>Laser Energy (mJ)</th>
<th>(L_{o1}) ((\AA))</th>
<th>(L_{o2}) ((\AA))</th>
<th>(\sigma_1) ((\AA))</th>
<th>(\sigma_2) ((\AA))</th>
<th>PL(_1) peak position (eV)</th>
<th>PL(_2) peak position (eV)</th>
<th>FWHM(_1) (eV)</th>
<th>FWHM(_2) (eV)</th>
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<tbody>
<tr>
<td>4</td>
<td>500</td>
<td>25</td>
<td>16.58</td>
<td>1.46</td>
<td>0.7</td>
<td>1.78</td>
<td>2.63</td>
<td>0.35</td>
<td>0.63</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>23.6</td>
<td>16.2</td>
<td>1.1</td>
<td>1</td>
<td>1.85</td>
<td>2.695</td>
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<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>24.2</td>
<td>15.8</td>
<td>1.2</td>
<td>0.55</td>
<td>1.814</td>
<td>2.805</td>
<td>0.26</td>
<td>0.55</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>24.6</td>
<td>16</td>
<td>1</td>
<td>0.6</td>
<td>1.805</td>
<td>2.741</td>
<td>0.25</td>
<td>0.58</td>
</tr>
<tr>
<td>6</td>
<td>700</td>
<td>25</td>
<td>18.76</td>
<td>1</td>
<td>0.4</td>
<td>1.78</td>
<td>2.311</td>
<td>0.32</td>
<td>0.24</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>24.2</td>
<td>16.6</td>
<td>1.6</td>
<td>1.5</td>
<td>1.814</td>
<td>2.555</td>
<td>0.40</td>
<td>1.26</td>
</tr>
</tbody>
</table>
Figure (3-14): PL spectra of silicon nanostructured films prepared with different target-to-substrate distances. The experimental PL data (dotted lines) are fitted with the quantum confinement model (solid lines) in the left column and the right column represents the corresponding Gaussian distribution used for PL fitting.
The first peak is shifted slightly towards shorter wavelengths, at ~ 1.8 eV. The second peak is shifted slightly towards shorter wavelengths, in the range 2.55 to 2.805 eV. This band was unambiguously attributed to a radiative recombination through defects in SiO₂ structure while 1.8 eV band was ascribed to quantum confinement mechanism [17].

**Effect of Laser Wavelength**

The intensity variations of the background signal are clear indications that the ablation depends on the laser wavelength, which governs the penetration depth of the laser beam, the temperature evolution, and the affected target volume. The shift of the PL band position might be a result of quantum size effect related to the size of nanocrystallites controlled by laser wavelength parameter.

Figure (3-15) shows the PL spectra of silicon nanoparticles prepared by pulsed laser ablation and different laser wavelengths of 532 and 1064 nm. These PL peak when the wavelength of pulsed laser is increased from 532 to 1064 nm, shifted toward lower energy from 1.76 eV (704.5 nm) to 1.78 eV (696.6 nm) for the first peak and from 2.283 eV (543 nm) to 2.311 eV (536.5 nm) for the second peak table (3-6).

The physical reason for this shift could be discussed as follows. The quantum confinement effect could explain that the bandgap of materials decreases as the size of quantum structure increases. This results in a green shift in optical luminescence energy [10]. Therefore, it could be expected that the nanocrystallite size increase by the increase of laser wavelength. Similarly,
with other semiconductors, the penetration depth of laser into silicon increases with the increase of wavelength in PLA. As the laser wavelength increases, there is more possibility that larger nanocrystallite could be formed on the substrate surface.

We have also investigated effects of deposition conditions on PL properties of Si NCs formed by PLA. The peak shifts with different preparation parameters and blue shifts show that the red PL band at \(~1.8\) eV is due to the QCE in Si NC cores. The second peak position relates the blue PL band at \(2.5-2.8\) eV to the localized surface states at the Si/SiO\(_2\) interface \[99\]. Several authors also described two PL bands in the blue-green and yellow-red ranges from Si \[96-98\]. They attributed the blue-green band to the carrier recombination at surface states or defects and the yellow-red band to the recombination of confined electron-hole pairs in Si NCs.

![Figure (3-15): The experimentally observed PL spectra of ablated Si-nc samples for different laser wavelength (discrete points) left column. The corresponding Gaussian distributions are given in the right column](image-url)
Table (3-6): The calculated nanocrystallite sizes of Si-nc samples prepared with different laser wavelength and the experimentally observed FWHM as well as PL peak position.

<table>
<thead>
<tr>
<th>Laser wavelength (nm)</th>
<th>( L_{o1} ) (Å)</th>
<th>( L_{o2} ) (Å)</th>
<th>( \sigma_1 ) (Å)</th>
<th>( \sigma_2 ) (Å)</th>
<th>PL(_1) peak position (eV)</th>
<th>PL(_2) peak position (eV)</th>
<th>FWHM(_1) (eV)</th>
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<td>0.45</td>
<td>1.76</td>
<td>2.283</td>
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<td>0.25</td>
</tr>
<tr>
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<td>25</td>
<td>18.76</td>
<td>1</td>
<td>0.4</td>
<td>1.78</td>
<td>2.311</td>
<td>0.32</td>
<td>0.24</td>
</tr>
</tbody>
</table>

3.4 Raman Spectroscopy Measurement

The vibrational properties of the silicon nanoparticles produced by laser ablation were investigated by examining Raman spectra. The transverse optical (TO) phonon line, from bulk silicon appears at 520 cm\(^{-1}\).

An important issue is whether Si nanoparticles are amorphous or crystalline. Direct evidence by AFM could not be obtained; however, we assume the Si particles are amorphous. In order to verify this hypothesis, we have grown a thick film of Silicon using thousands of pulses or annealing by laser and investigated by Raman spectroscopy. The obtained Raman spectrum is presented in figure (3-16) for YAG Laser 1064 nm, E= 700 mJ, \( d_{r,s} = 0.6 \) cm, No. of pulses (a) 30 (b) 20. It clearly shows that the deposited material is amorphous film [7].

Raman spectroscopy is an efficient technique to evaluate quantitatively measurements of stress, presence of nanocrystals and homogeneity. Si crystals have typical characteristics of strength emission and narrow band at (520 cm\(^{-1}\)), suggesting that they contain small amounts of nanocrystalline
silicon (nc-Si) because the phonon confinement in nc-Si should be different from that in amorphous Si [12], which corresponds to transverse acoustic mode in first order. However in the case of amorphous silicon, the lack of order induces modifications in the vibrational density of states and in this case the Raman spectrum is characterized by two faint and broad bands at (150 cm\(^{-1}\)) and (480 cm\(^{-1}\)) [100].

![Raman spectra of Si nanoparticles thin film on glass](image)

Figure (3-16): Raman spectra of Si nanoparticles thin film on glass
3.5 Structural properties

Formation of thin films by PLA is a process that depends on many material parameters such as density, kinetic and potential energies, ionization degree, and type of the condensing particles, as well as the temperature and physicochemical properties of the substrate. It is known that noble metals and noble gases have high rates of surface diffusion and crystallize readily from the vapor source even at low substrate temperatures. In contrast, silicon and most other semiconductors have lower rates of surface diffusion; therefore, crystalline films are very difficult to grow [101].

The X-ray beam is diffracted at specific angular positions with respect to the incident beam depending on the phases of the sample. When crystal size is reduced toward nanometric scale, then a broadening of diffraction peaks is observed and the width of the peak is directly correlated to the size of the nanocrystalline domains (Debye-Scherrer relation) [85].

Figures (3-17) presents the corresponding variations in the XRD diagram at different incident laser energy. Due to changes in the film in the previous step, the amount of nc-Si in the film decreases, accompanying an obvious increase in the amount of amorphous silicon.
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Figure (3-17): The XRD spectra of the samples prepared at different laser energies. 
$[\lambda_{\text{Laser}} = 1064 \text{ nm}]$
The x-ray diffraction of the deposited films exhibits completely different spectra. As shown in Figure (3-17c), there are two peaks; the broad peak is related to the nanoparticle sizes in the amorphous (a-Si) deposited film. While the second peak represents the large size droplet particles abundant in the deposited film. These droplets are considered as crystalline silicon of plane (111) at the scattering angle of (29°)

3.7 The Surface Morphology

A. The AFM of the Si nanaoparticles thin films

The atomic force microscope produces topological images of surfaces at very high magnification and it is even possible to observe the atomic structure of crystals. The aim of this study with the atomic force microscope is to obtain information about the formation about the surface.

The islands formed on the substrates surface start to coalescence and new small islands start to grow between the bigger islands. A certain thickness of the films are formed, which transform the growth mode into the pseudo-two-dimensional grow, and therefore leads to a high surface roughness.

The rough surface systematically observed on the deposits is not the result of droplets directly transferred from the Si target, but is due to the formation of aggregated particles.
1. Effect of number of pulses

The surface morphology of the laser-ablated films has been subjected to extensive study. Figure (3-18) shows the surface evolution with increasing the number of pulses from (5-30) pulses. It has been observed that the particles density increases proportionally with the number of pulses. Those particles have different sizes, the large particle size is found at the spot edge. This is due to the Gaussian distribution of the pulsed laser energy. Increasing the number of laser shots to (30) pulses increases the number of particles condensed on the substrate.

The increase in the particle's number is probably related to the increase in the number of laser pulses. It is clear that the particles become much closer to each other. The particle density becomes greater as compared with the previous case, where the particles begin to agglomerate with different sizes creating thin Si film.

One of the goals in this work is to correlate the number of nanoparticles seen in AFM images with the number of laser pulses. In general, we saw that the number of nanoparticles increases with the number of pulses. However, this relation is not a straight line, due to two major reasons. The first is as mentioned before, each experiment was performed on different samples. The second is that the density of the deposited Si particles is not uniform within the same sample. It is well known that deposited films obtained by PLA method are not homogenous in thickness and the films are thicker in front of the center of the plume. Therefore, a higher population of nanoparticles at this particular position is expected.
Figure (3-18): The 2D, cross section and 3D AFM images of Si nanoparticles samples prepared under different numbers of laser pulses (A) 5 (B) 10 (C) 20 & (D) 30 laser pulses. [\lambda_{\text{Laser}} 1064 \text{ nm}, E=700 \text{ mJ}, d_{\text{sl}}=\cdot.6 \text{ cm}]
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The energetic particles of the plume arriving the glass substrates produce defects on its surface, due to nuclear stopping, and make the tetrahedral network structure. Therefore, it is energetically favored for the arriving Si species to spread uniformly in the substrate surface, as it is shown by the rather small average roughness increase after increasing number of pulses.

With increasing number of laser pulses, surface roughening and formation of “soft” agglomerates occurred as shown in Figure (3-18), and a columnar structure started to develop.

AFM technique uses a laterally moving tip, while the cantilever reflects the samples different from the topography height Z, or the Z measurements as shown in Figure (3-18) (middle column). Although the tip is very sharp, it is impossible to gather the information from the underside of the specimen.

Table (3-7) illustrates the effect of the number of pulses on the average surface roughness. The surface roughness increases then decreases due to the additional ejected particles when increasing the number of pulses and these particles cover the surface cavities leading to decrease in the surface roughness.
Table (3-7): The calculated average roughness of Si-nc samples prepared with different number of pulses $[\lambda_{\text{Laser}} ~ 1064 \text{ nm}]$

<table>
<thead>
<tr>
<th>Number of pulse</th>
<th>Average Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.555</td>
</tr>
<tr>
<td>10</td>
<td>4.726</td>
</tr>
<tr>
<td>20</td>
<td>2.900</td>
</tr>
<tr>
<td>30</td>
<td>2.864</td>
</tr>
</tbody>
</table>

Figure (3-19) show the histogram for the distribution density (left column). A distribution of the function values is set for this size, the position of the central point in this distribution is determined and the grain size analysis varying across the film (right column).

Our results show the particle density across the film. since larger size particulates have the higher angular distribution, we have observed that number of larger particles increased with the number of pulses This could be attributed to the increasing amount of the ejected particles reaching the substrate surface, as shown in Figure (3-19 left column)

Figure (3-19 right column) large particles with an irregular shape and sizes up to ~3 microns are observed on the surface of all films, but their number is very low. These particles are probably the fragments of the target material ejected at the very first stages of the ablation.
Figure (3-19): On the left column, histogram is the function values distribution density. On the right column is a size values distribution of Si nanoparticles samples prepared under different number of pulses (A) 5 (B) 10 (C) 20 & (D) 30 pulses.
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2. Effect of laser energy

Laser energy has a significant effect on the surface morphology. This effect is prominent in Figure (3-20), where the difference in particle size and size distribution to the ablated particles with increasing laser energy is easily recognized.

The particle size clearly increases as the laser energy increases from 300 to 600 mJ. Particles in this size range exhibit strong quantum confinement effects, with experimentally predicted bandgap ranging from 2.61 – 2 eV. Size distributions are relatively narrow, with standard deviations of approximately few nm for all energy densities. This increase in particle size may be qualitatively understood because the amount of material removed from the target and the plume density increases with increasing pulse energy. Collisions between Si atoms or small clusters will occur more frequently, resulting in larger particles. It must be noted that a significant number of smaller (nm) nanoparticles are produced at even the highest energy densities employed. This may result from particles that have not yet completed their growth in the plume [102].

The sample prepared at (300 mJ) laser energy shows limited number of particles. These particles are randomly distributed over the substrate area; figure (3-20A). One can see, these particles have almost large sizes. That is attributed to the few numbers of particles reach the substrate surface due to the low laser energy, which causes ablation of low particles numbers of large sizes. When laser energy increases to (400 mJ), it was found that the particle number increased. The figure reveals the appearance of small particle sizes distributed within the unit area as shown in Figure (3-20B).
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The representative micrographs shown in figure (3-20 C & D) of the deposited nanoparticles film produced at (500 mJ) and (600 mJ) respectively show an increasing particles density with higher laser energy. As can be seen, the ablated particles create a thin film on the substrate surface due to increasing the abundance of these ejected particles with the laser energy, therefore, large amount will have high energy, which allows them reaching the substrate area and condensed. It is obvious from the results above that the particles distribution can be controlled by varying the incident pulsed laser energy. Beside these nanoparticles, the micron size particles can also be seen in the micrograph shown in figure (3-20). These random shaped micro particles are formed by the particulate material ejected from the target.

Table (3-8) gives the average roughness obtained for various laser energies. When employing laser energies from 300 to 500 mJ, the average roughness increases with increasing laser energies, but at higher laser energy 600 mJ the average roughness decreases almost less than three times from the film prepared at 500 mJ. This is due to the increased laser power density and consequently the number of small nanoparticles. More probably, as the incident laser energy increases, the amount of the absorbed energy in the target increases which leads to an increase in the ejected particles toward the substrate filling the cavities at the surface.
Figure (3-20): AFM images 2D, cross section [Z(nm) vs. X (nm)] and 3D of Si nanoparticles samples prepared under different laser energies: (A) 300, (B) 400, (C) 500, & (D) 600 mJ [\textit{\lambda}_{\text{Laser}} 1064\text{ nm}, d_{f-s} = .4\text{ cm}, \text{ No. of pulses} = 30]
Table (3-8): The calculated average roughness of Si-nc samples prepared with different laser energy [\( \lambda_{\text{Laser}} = 1064 \text{ nm} \)]

<table>
<thead>
<tr>
<th>Laser energy (mJ)</th>
<th>Average Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>8.979</td>
</tr>
<tr>
<td>400</td>
<td>10.092</td>
</tr>
<tr>
<td>500</td>
<td>20.824</td>
</tr>
<tr>
<td>600</td>
<td>7.335</td>
</tr>
</tbody>
</table>

Figure (3-21) shows the histogram of the distribution density (left column).

It is clear from figure (3-21) to distinguish the effect of increasing the laser energy from 300 to 600 mJ. Size distribution and the average size decrease since the higher laser energy leads to increasing the laser power density and consequently the number of smaller nanoparticles, as shown in figure (3-21D).
Figure (3-21): On the left column, histogram is the function values distribution density. On the right column is a size values distribution of Si nanoparticles samples prepared under different laser energies (A) 300 (B) 400 (C) 500 & (D) 600 mJ [$\lambda_{\text{Laser}} = 1064 \text{ nm}$]
Figure (3-22) shows the AFM images of the nanoparticles films prepared under different laser energies at a wavelength (532 nm); this wavelength produces smaller size of nanoparticles. For the wavelength (1064 nm), we found that larger sizes were produce compared with those produced by wavelength (532 nm). Figure (3-22) shows a cross section represent the relation between height Z (nm) and the scanning in the plane x-axis (nm) of the deposited nanoparticles film produced at laser energy 300 to 600 mJ we show at 500 and 600 mJ have rougher surface decreases when increasing the laser energy.

Films ablated by 1064 nm have rougher surface and larger particles with height up to 800 nm compared to 532 nm, figure (3-22) and lower average roughness as given in tables (3-8) and (3-9) respectively. However, according to AFM images, the observed particles do not lay on the surface; they seem to be embedded in the film.
Figure (3-22): AFM images 2D, cross section [Z(nm) vs. X (nm)] and 3D of Si nanoparticles samples prepared under different laser energies (A) 300 (B) 400 (C) 500 & (D) 600 mJ [$\lambda_{\text{laser}} =$532 nm]
Chapter Three: Results and Discussion

Table (3-9) shows the effect of laser energy on the average roughness. The surface roughness at a wavelength of (532 nm), decreases with increasing laser energies and this due to the continuous filling of the surface cavities that leads to a reduction in the surface roughness.

Table (3-9): The calculated average roughness of Si-nc samples prepared with different laser energy [\(\lambda_{\text{Laser}} = 532 \text{ nm}\)]

<table>
<thead>
<tr>
<th>Laser energy (mJ)</th>
<th>Average Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>10.680</td>
</tr>
<tr>
<td>400</td>
<td>8.566</td>
</tr>
<tr>
<td>500</td>
<td>6.976</td>
</tr>
<tr>
<td>600</td>
<td>4.247</td>
</tr>
</tbody>
</table>

Figure (3-23) illustrates the effect of laser energies at wavelength 532 nm on the distribution density (left column) and average size values distribution (right column) of Si nanoparticles. The mean size distribution decreases with increasing the laser energy. This could be interpreted as the amount of the absorbed energy in the target increases, leading to an increase in the ejected particles toward the substrate. (Same behavior found in laser wavelength 1064 nm).

The right column indicates that the average sizes for smaller particles increases with increasing laser energies.
Figure (3-23): On the left column, histogram is the function values distribution density. On the right column is a size values distribution of Si nanoparticles samples prepared under different laser energies (A) 300 (B) 400 (C) 500 & (C) 600 mJ \([\lambda_{\text{Laser}} = 532\text{nm}]\)
Effect of target-to-substrate distance

Figure (3-24) illustrates the effect of varying the distance between target and the substrate on the particle's density and size. This figure reveals that very small size particles could be recognized when we increase the distance between target and substrate.

The sample prepared at very small target-substrate distance (0.4 cm), figure (3-24A), and shows that the film contains almost large particles randomly distributed over the substrate. The presence of different particle sizes in small target-substrate distance is related to the fact that almost all the ejected particles will reach the substrate. The ablated particles do not necessarily have high energy to reach the substrate because of small distance. The presence of large particle size is found to be concentrated on the edge of the substrate; may be explained by the Gaussian distribution of the laser pulse, which produces higher temperature at the center and lower at the laser-target interaction region. Therefore, large particle sizes of the molten material exist at the film edges while small particle sizes of the vaporized material are abundant at the center.

When the target-substrate distance increased to (0.6 cm), a limited number of particles are distributed over the substrate surface as illustrated in figure (3-24B). The sizes of these particles are varied from small sizes and large sizes spreading homogeneously on a wide area of the substrate. The increase in the distance reveals that no large particles reach the substrate, where these particles are heavy to do so. The increase in the particles density leads to an increase in the number of particles and droplets reaching the substrate at this distance. It is suggested that when target-to-substrate distance
increases, a plume is generated and expands away from the target, allowing for an efficient spread of the particles over the substrate as shown in figure (3-24C).

Figure (3-24C), illustrates the sample prepared at (0.8 cm) distance. One can clearly see from this image that a very small particles spread on the substrate. Our observation indicates that the target-to-substrate distance is an excellent parameter for tuning the particle size to the desired range.

Figure (3-24): AFM images 2D, cross section \([Z(\text{nm}) \text{ vs. } X(\text{nm})]\) and 3D of Si nanoparticles samples prepared under different target-to-substrate distances \((d_{t-s})\) (A) 0.4 (B) 0.6 & (C) 0.8 cm [\(\lambda_{\text{Laser}} = 1064 \text{ nm}, E = 700 \text{ mJ}, \text{No. of pulses}= 20\)]
At long distances, an almost regular macroscopic pattern was developing as shown in figure (3-24). Histograms of the function values distribution density of the Si NPs measured from the topographic images are shown in figure (3-25).

The average roughness at different target-to-substrate distances as given in table (3-10), where the average size results show the average film roughness for the films produced at 0.6 cm as compared to those produced at 0.4 cm and 0.8 cm. This implies that 0.6 cm distance produces a silicon film, which has a large amount of smaller sizes leading to a reduction in the surface roughness. This result can be explained by the large particle sizes present in the sample prepared at very small target-to-substrate distances at 0.4 cm. These large particles disappear or are hardly observed at 0.6 cm. Since large particles have smaller kinetic energy, these particles could not reach the substrate.

<table>
<thead>
<tr>
<th>(d_{t-s}) (cm)</th>
<th>Average Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>7.023</td>
</tr>
<tr>
<td>0.6</td>
<td>2.900</td>
</tr>
<tr>
<td>0.8</td>
<td>6.445</td>
</tr>
</tbody>
</table>
Figure (3-25) describes the distribution density (left column) and frequency size values distribution (right column) under different distances between the target and the substrate. The histogram of the size distribution density for high counts changes from 117, 106 and 35 nm, which is inversely proportional to the target-to-substrate distances at 0.4, 0.6 and 0.8 cm respectively. This is probably attributed to the increase of the mean free path of the ablated particles. Therefore, only smaller particles of higher kinetic energy can reach the substrate surface at long distance (0.8 cm). The amount of the molten material ejected from the target is larger at short distance (0.4 cm) giving greater average film sizes.

The right column represents the frequency of the average sizes for films prepared with different target-to-substrate distances.
Figure (3-25): On the left column, histogram is the function values distribution density. On the right column is a size values distribution of Si nanoparticles samples prepared under different target-to-substrate distances (A) 0.4 (B) 0.6 & (C) 0.8 cm.

The AFM images of the surface of the thin films are represented in figure (3-26) with a magnification of (1μm×1μm) prepared at a laser wavelength of 532 nm and at different target-to-substrate distance (0.4 cm and 0.6 cm). Table (3-11) gives the average roughness for two target-to-substrate distances we shown are increasing target-to-substrate distance due to
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reduction surface roughness because of only smaller particles have of higher kinetic energy can reach the substrate surface at long distance.

![AFM images 2D, cross section [Z(nm) vs. X(nm)] and 3D of Si nanoparticles samples prepared under different target-to-substrate distances (A) 0.4 and (B) 0.6 [λ_{Laser}=532] 1 μm×1 μm](image)

Table (3-11): The calculated average roughness of Si-nc samples prepared with different target-to-substrate distances [λ_{Laser}=532 nm]

<table>
<thead>
<tr>
<th>d_{ts} (cm)</th>
<th>Average Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>3.882</td>
</tr>
<tr>
<td>0.6</td>
<td>1.625</td>
</tr>
</tbody>
</table>
Figure (3-27) describes the distribution density values (left column) and frequency size values distribution (right column) under different distances between the target and the substrate at laser wavelength of 532 nm and a magnification of (1μm×1μm). It shows a maximum distribution density of 20 nm at 0.4 cm distance and 13 nm at 0.6 cm distance. This indicates that smaller nanoparticles could be collected at the distance 0.6 cm.

![Graph A](image1.png)
![Graph B](image2.png)

**Figure (3-27):** On the left column histogram is the function values distribution density. On the right column is a size values distribution of Si nanoparticles samples prepared under different target-to-substrate distances (A) 0.4 and (B) 0.6

4. Effect of laser wavelength

The formation process of films produced at 1064 nm by PLA was studied. IR-generated plasma consists of large fragments and solidified droplets, thus, films with rough surface are formed.
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The laser wavelength has also an effective role on the final morphology of the microstructures. In this section, the second harmonic wavelength of the IR 1064 nm laser light has been used to examine how laser radiation with a central wavelength of 532 nm affects the surface morphology. Figure (3-28) shows the evolution of the silicon film surface irradiated by laser pulses. The development follows the same progression as those made with (1064 nm).

The surface of the thin films was previously analyzed with AFM, and the images are presented in figure (3-28) for two laser wavelengths. Comparison of this series of images with the images made by Scanning Electron Microscope (come later) shows that the general trends are the same: films ablated at 1064 nm have rougher surface compared to those ablated at 532 nm.

Figure (3-28): AFM images 2D, cross section [Z(nm) vs. X(nm)] and 3D of Si nanoparticles samples prepared under different laser wavelength

(A) \( \lambda_{\text{Laser}} = 1064 \text{ nm} \) and (B) \( \lambda_{\text{Laser}} = 532 \text{ nm} \)
Figure (3-29) indicates that the shorter wavelength (532 nm) produces smaller nanoparticle sizes, less than 85 nm. This result is in constant agreement with those of PL and the transmission spectra.

Figure (3-29): On the left histogram is the function values distribution density. On the right is a size values distribution of Si nanoparticles samples prepared under different laser wavelength (A) $\lambda_{\text{Laser}}=1064$ nm and (B) $\lambda_{\text{Laser}}=532$ nm
Table (3-12) summarizes the general trends of the observed morphology characteristics determine by AFM of thin film Si nanoparticles on glass substrate produced by nanosecond PLA at different parameters. The table demonstrates effects of laser parameters on the film morphology parameters such as the column height, density and the grain size. It is found that increasing the laser wavelength and number of pulses lead to an increase in the overall morphology parameters, while the laser energy and the target-to-substrate distances play different role with morphology parameters. Increasing the laser energy decreases the grain size, which attributes to the generation of higher thermal energy and subsequently the amount of the ablated smaller particles. In addition, increasing target-to-substrate distances due to only smaller particles have of higher kinetic energy can reach the substrate surface at long distance.

<table>
<thead>
<tr>
<th>Observables</th>
<th>Parameter</th>
<th>Morphology Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Height</td>
<td>Density</td>
</tr>
<tr>
<td>Number of pulses</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Laser energy</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Target-to-substrate distances</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Laser Wavelengths</td>
<td>↑</td>
<td>↑</td>
</tr>
</tbody>
</table>
B. The SEM of the Si nanoparticles thin films

The AFM technique uses a laterally moving tip, while the cantilever reflects the sample's topography, or the z measurements. Even though the tip is very sharp, it is impossible to gather the information from the underside of the specimen. The spherical particle will be viewed as a bump by the Atomic Force Microscope. To correct the AFM image for this effect some deconvolution techniques are used. In conclusion, the AFM and SEM images are complementing each other.

Figure (3-30) shows the scanning electron micrographs of the Si nanoparticles films grown on glass substrates. Few droplets have been observed, which is generally assumed to be the consequence of thermal effects during the laser-matter interaction; liquid material being ejected as droplets from the molten zone of the irradiated target. The droplets are generally observed in films grown by nanosecond PLA.

Silicon and most other semiconductors have lower rates of surface diffusion; therefore, crystalline films are very difficult to grow [103].

The surface morphology of the samples was also observed by AFM where a much more dense distribution of nanoparticles was evident with respect to the relative SEM images.
Figure (3-30): SEM images showing Si nanoparticles for different number of pulses. (a) 5 (b) 10 (c) 15 & (d) 30 pulses $[\lambda_{\text{Laser}} = 1064 \text{ nm}, E = 700 \text{ mJ}, d_{\text{gas}} = 0.6 \text{ cm}]$

One of the main limitations of PLA is the generation of particulates. In general, ultrafine particulates are not considered as a problem for the PLA formed films. However, large particulates having diameters in the micron range can be a serious problem for the thin film applications. Therefore, it is essential to know the nature, the size, and the area density of the particulates on the film surface.

The droplets of material figure (3-31) are formed from the target as a consequence of transient melting of the subsurface and expelled by the recoil of the shockwave. These droplets can be avoided at pressures in the torr
regime largely by positioning the collection substrate off the vapor plume axis and relying on the higher diffusion mobility of the smaller particles for deposition [103].

However, redeposition does not explain why the spherical balls are only present for stationary samples. We speculate that the varying laser energy at each point on the surface during translation melts the spherical ball tips. However, the intensity of these pulses is not constant as the Gaussian profile of the beam passes over a spot. That is, a given spot on the surface is first struck by the leading edge of the Gaussian beam, which is at lower laser energy than the center of the beam.

![Figure (3-31): SEM micrographs of the deposited Silicon droplets](image)

The nanoscale particles on the translated samples are redeposited material from the ejected plume. For each irradiated spot, there is a ring of material around the spot. On a stationary sample, all of this debris lie away from the area where microstructures form.
Figure (3-32) represents the SEM imaging of the observed nanoparticles for Si film deposited by PLA. The observed structure for that film is dense and the particles are uniformly distributed in the film with increasing laser energy from 500 to 700 mJ. The average particle size is in the nano regime.

Figure (3-32): SEM images showing Si nanoparticles prepared under different laser energies [$\lambda_{\text{Laser}} = 1064$ nm, (d) $E=500$ & (e) 700 mJ, $d_{s} = 0.4$ cm, No. of pulses=20]

Figure (3-33) shows scanning electron micrographs of the as-deposited films prepared by direct deposition in the ablation chamber. The glass substrates were placed at different positions from the target. The film
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generated at $2 \times 10^{-4}$ Torr showed a rough surface structure composed of particles with diameters ranging from few to a few hundred nanometers.

Figure (3-33c), SEM micrograph of the deposited Si film in vacuum for 0.8 cm distance, reveals the creation of very uniform thin film without any droplets formation. Only droplet of redeposited silicon appear at the top of the thin film whose characteristic dimension is typically a few hundreds of nanometer.

Figure (3-33): SEM images showing Si nanoparticles prepared under different target-to-substrate distances. [$\lambda_{\text{Laser}} = 1064$ nm, $E = 700$ mJ, $d_{\text{ts}} = (a) 0.4$ (b) 0.6 & (c) 0.8 cm, No. of pulses = 20]
In the high-magnification SEM images, the surface of each particle showed a substructure composed of smaller particles. This suggested that the particles were agglomerates generated by the collision of primary particles on the substrate, rather than droplet-like particles generated by the liquid phase splash induced by the impact of the laser pulse. On the other hand, the film prepared under different parameters had a rather uniform structure, in spite of the broad size distribution in its microstructure seen in the high-magnification image.

The films are observed to be formed from a more or less uniform layer with spherical and randomly particles. Laser ablation of materials results inevitably in the formation of debris due to the volume of the material which is removed by the laser beam. The presence of particles due to the so-called the debris consists of nanoparticles phenomenon is one of the major pulsed laser ablation (PLA) techniques [77].

The surface of the thin films was analyzed with SEM, and the images are represented in Figure (3-34) in three magnifications.
Figure (3-34): SEM images showing Si nanoparticles prepared at different magnification \( \lambda_{\text{Laser}} = 1064 \text{ nm}, E = 700 \text{ mJ}, d_{s} = 0.4 \text{ cm}, \text{No. of pulses} = 20 \) (1,500 X, 15,000 X and 30,000 X magnification, planar view)
Effect of laser wavelength

It is found that the density of the particles is higher for the sample prepared at 1064 nm from that prepared at 532 nm as shown in figure (3-3). Most of the particulates observed have spherical shapes, and most probably refer to the solidified liquids droplets ejected from the target due to superheating of the subsurface region.

The nature of the ablation process was discussed in (Chapter 2). IR-ablation is primarily a volume process, and, therefore, it is more likely that the subsurface gets heated before the surface reaches the vaporization temperature. Consequently, more particles are ablated with 1064 nm light. The 1064 nm line penetrates deeply into the target, leading to a tremendous temperature rise in a large volume of the material.

The ablation with the visible light is a surface process; only several atomic layers are affected. Therefore, atoms and molecules are ablated from the target surface. Even if larger particles are ejected, they are eventually reduced in size by the high photon energy of the incoming laser pulse.
Figure (3-3a): SEM surface images of PLA Si nanoparticles films on glass formed at:
(a) $\lambda_{\text{Laser}} = 532 \text{ nm}$ (b) $\lambda_{\text{Laser}} = 1064 \text{ nm}$ [E= 700 mJ, $d_{s} = 0.4 \text{ cm}$, No. of pulses= 20]
4.1 Conclusions and Perspectives

With respect to the outgoing results, the following conclusions can be made:

1. The optical spectra (transmittance and reflectance) showed systematic changes correspond to their nanostructures.

2. The magnitude of the refractive index was found to change linearly with the size reduction of the nanoparticles.

3. The energy dependent absorption coefficient was calculated from optical spectra to determine bandgap ($E_g$). This parameter was found to increase with the decrease of the confined dimension of the nanostructures.

4. The photoluminescence (PL) spectra at RT revealed a broadband spectrum in a range of 400 nm to more than 700 nm and the position and shape of PL spectra depend on nanocrystal size and size distribution.

5. The electron confinement model gave a good matching with the experimentally observed PL spectra since the model could appropriately include the effects of the nanocrystallite size distribution.

6. XRD analysis and Raman spectroscopy confirmed that silicon nanoparticles prepared in this research are amorphous in nature.
7. The morphological study of the deposited thin film that is revealed from the AFM analysis shows that the films have a granular structure with the constituting silicon nanoparticles. The film roughness depends on different parameters and can be controlled accordingly.

8. Results show that the film morphology could be controlled by different parameters like laser energy, laser wavelength and number of pulses as well as the target-to-substrate distances.

9. The SEM images show a mixture of nanoparticles and droplets due to the melting and evaporation processes.

4.2 Suggestions for Future Research

1. To make use of the properties of the nanometer-range structural regularity of Si nanoparticles, we need to develop and utilize some things such as temperature substrate or insert gas for films spheres, which can maintain their sizes, and shapes that would assist pulsed laser ablation (PLA).

2. Utilize Si nanoparticles films for many applications, for example, photoelectric devices, such as sensor arrays and solar cells.
### List of Symbols & Abbreviations

<table>
<thead>
<tr>
<th>S.&amp;A.</th>
<th>Meaning</th>
<th>S.&amp;A.</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Absorption Coefficient</td>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>a-Si</td>
<td>Amorphous Silicon</td>
<td>$h\nu$</td>
<td>Photon Energy</td>
</tr>
<tr>
<td>L</td>
<td>Angular Momentum</td>
<td>h</td>
<td>Plank's Constant</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>$R_a$</td>
<td>Average Roughness</td>
<td>QCE</td>
<td>Quantum Confinement Effect</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction Band</td>
<td>QDs</td>
<td>Quantum Dots</td>
</tr>
<tr>
<td>$L_x$</td>
<td>Confined Region in X-axis</td>
<td>n</td>
<td>Quantum Number</td>
</tr>
<tr>
<td>$L_y$</td>
<td>Confined Region in Y-axis</td>
<td>$R$</td>
<td>Reflectance</td>
</tr>
<tr>
<td>$L_z$</td>
<td>Confined Region in Z-axis</td>
<td>$n$</td>
<td>Refractive Index</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>$R(L)$</td>
<td>Distribution Size</td>
<td>$R_q$</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>EMA</td>
<td>Effective Mass Approximation</td>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>$m_e^*$</td>
<td>Effective Mass for Electrons</td>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>$m_h^*$</td>
<td>Effective Mass for Holes</td>
<td>$\sigma$</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>$m_e$</td>
<td>Electron Mass</td>
<td>$d_{ts}$</td>
<td>Target-to-Substrate Distance</td>
</tr>
<tr>
<td>EPM</td>
<td>Empirical Pseudopotential Method</td>
<td>$a_1, a_2$</td>
<td>Temperature-Dependent Constants</td>
</tr>
<tr>
<td>ETB</td>
<td>Empirical Tight-Binding Method</td>
<td>$\gamma$</td>
<td>The Coupling Constant</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Energy Bandgap</td>
<td>e</td>
<td>The Electric Charge of the Electron</td>
</tr>
<tr>
<td>$E_g^0$</td>
<td>Energy Bandgap of Bulk Silicon</td>
<td>$\Delta x$</td>
<td>The Fringe Spacing</td>
</tr>
<tr>
<td>$E_{g[nano]}$</td>
<td>Energy Bandgap of Nanoscale Silicon</td>
<td>x</td>
<td>The Fringe Width</td>
</tr>
<tr>
<td>k</td>
<td>Extinction Coefficient</td>
<td>c</td>
<td>The Intensity of the Light Source at the Excitation Energy (PL)</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
<td>$\varepsilon_\infty$</td>
<td>The permittivity Constant of Vacuum</td>
</tr>
<tr>
<td>d</td>
<td>Grain Size</td>
<td>$\varepsilon_r$</td>
<td>The Relative permittivity Constant</td>
</tr>
<tr>
<td>$m_h$</td>
<td>Hole Mass</td>
<td>t</td>
<td>Thickness</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocrystal</td>
<td>$\eta$</td>
<td>Transition Electronic</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
<td>T</td>
<td>Transmittance</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infrared</td>
<td>TO</td>
<td>Transverse Optical</td>
</tr>
<tr>
<td>Nd-YAG</td>
<td>Neodymium-Yttrium-Aluminium-Garnet</td>
<td>VB</td>
<td>Valance Band</td>
</tr>
<tr>
<td>L</td>
<td>Particle Diameter</td>
<td>VIS</td>
<td>Visible</td>
</tr>
<tr>
<td>Z</td>
<td>Particle height</td>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>$R_o$</td>
<td>Particle Radius</td>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
References

5. L. Brus, “Semiconductor Nanocrystal”, Published January (1998); WTEC Hyper-Librarian


31. “Quantum Dot Lasers”, Published: September 1999; WTEC Hyper-Librarian
32. D. Jena, “Bandstructure in Low-Dimensional Structures”, University of Notre Dame (Fall 2004)
47. S. S. Jan, “Production of Porous Silicon by Laser-Induced Etching” Thesis (M.Sc), Applied Science Department, University of Technology (2006).


61. P. Me´linon, P. Ke´gle´lian, B. Pre´vel, V. Dupuis, A. Perez, B. Champignon, Y. Guyot, M. Pellarin, J. L. Rousset and P. Deliche´re,


