Chapter - 1
Introduction

1.1 Motivation

Being the workhorse of semiconductor industry silicon has been considered as a material of perpetual choice in making solar cells during last few decades as silicon is naturally abundant, environmentally inert and the generation of electricity from silicon solar cells is safe and effective, they do not produce the toxic air or emit greenhouse gas. In search for the suitable all-silicon solar cells, lots of attempt on research, development, optimization and commercialization has been performed for few decades beginning from the first generation photovoltaic technology to the third generation. First-generation photovoltaic technologies based on bulk silicon wafers are booming recently and are likely to continue their strong position over the next decade.\textsuperscript{1-5} Second-generation thin film photovoltaic technology has an attraction recently because of its potential for reduction in material costs.\textsuperscript{6-9} The “third-generation” approaches aim to leverage an additional decrease in the cost of photovoltaic electricity from “thin film” second generation technologies by increasing the efficiency dramatically.\textsuperscript{10-13} The effects of increased efficiency and low cost thin film processes have the potential to reduce costs per Peak Watt (Wp) of generating electricity very significantly.

In achieving high efficiency solar cells at low production cost (i.e. third generation solar cells), significant attempts have been made by several researchers on the evolution of new technologies and materials. In that direction the tandem structure solar cell can boost the efficiency progressively by stacking more cells on top of one another with the utilization of the extended solar spectrum.\textsuperscript{14-16} Cells made from multiple absorber materials have multiple optical band gaps. So, it will respond to multiple light wavelengths and some of the energy that would otherwise be lost to relaxation as described above, can be captured and converted. The band gaps for the each absorber layer will be in the decreasing order from the top cell to the bottom one, in order to absorb the photon in the efficient way. Apart from tandem cells, a number of more ‘paralleled’ approaches have also been suggested capable of similar efficiency to an infinite stack of tandem cells e.g. hot-carrier solar.\textsuperscript{17, 18} The principal concept underlying the hot carrier solar cell is to slow the rate of photoexcited carrier cooling to allow time for the carriers to be collected whilst they are still at elevated energies (‘hot’), and thus allowing higher voltages to be achieved from the cell.\textsuperscript{19} This requires
an absorber material in which carrier cooling is reduced from the picosecond timescale towards the radiative recombination timescale of nanoseconds. Significant reduction in cooling has been observed at very high illumination intensities via a ‘phonon bottleneck’ mechanism, which has been demonstrated to be enhanced in quantum well (QW) nanostructures. In order to reduce the illumination intensities at which this mechanism gives significantly slower cooling, towards one sun intensities, it is necessary to block the decay of optical phonons into acoustic phonons. In addition to an absorber material that slows the rate of carrier relaxation, a hot carrier cell must allow extraction of carriers from the device through contacts which accept only a very narrow range of energies (energy selective contacts or ESC). This is necessary in order to prevent cold carriers in the contact from cooling the hot carriers, i.e. the increase in entropy on carrier extraction is minimized. In tandem structure solar cells or in hot carrier solar cells, the band gap of each layers (e.g. n-/p-type window layer, absorber i-layer, energy selective contacts etc.) need to be tailor-made without compromising the charge-carrier transport in the layers. In order to achieve such, self-assembled and spontaneously grown silicon nano-crystals (Si-nc) embedded in doped/un-doped amorphous dielectric matrix of silicon e.g. amorphous Si (a-Si), amorphous silicon carbide (a-SiC<sub>x</sub>), amorphous silicon oxide (a-SiO<sub>x</sub>) and amorphous silicon nitride (a-SiN<sub>x</sub>) or in a super-lattice structures is attractive area of research in the field of material science for their potential applications as different layers in solar cells.

In that consideration, formation of Si-ncs or Si-QDs in doped and un-doped dielectric amorphous matrix (a-SiO<sub>x</sub>, a-SiC or a-SiN) or in multi-layer structure can be accomplished by plasma enhanced chemical vapor deposition (both capacitively and inductively coupled), hotwire CVD or RF magnetron sputtering. However, most of the available reports considered a two steps process which includes deposition of the an amorphous layer of silicon or silicon rich dielectrics of oxide, carbide and nitride followed by an essential high temperature (~1100 °C, in general) post-deposition annealing to felicitate the crystallization in the silicon network. This inevitable high temperature annealing step imposes a persistent hindrance in its successful application in thin film solar cells and restriction on the use of low cost substrates, and also affects the other pre-deposited layers of the device. In addition to that, the high temperature annealing process is an uncertain process in controlling the size of the silicon nano-
crystals and for the doped films or super-lattice films; the doping atoms might be diffused in an indefinite way in the films during the annealing process.

Also from technological point of view, a high deposition rate should be an important factor. Generally nanocrystalline silicon thin films have been developed with high H$_2$ dilution to the SiH$_4$ plasma. If deposited by the RF-PECVD method using hydrogen dilution, the formation of silicon nanocrystals requires higher RF-power density and temperature than those applied in amorphous silicon thin films preparation, owing to need to enhance atomic hydrogen density and available thermal energy which help nano-crystallization. High RF power and high hydrogen dilution are two critical parameters which facilitate nano-crystallization by increasing the atomic hydrogen density in the plasma. But higher RF power causes surface damage by high-energy ion bombardment and higher dilution retards the film growth rate, both of which are unfavourable from the device point of view. High deposition temperature again is not compatible with device fabrication. Very-high frequency (VHF), ultra-high frequency (UHF), microwave (MW), inductively coupled plasma (ICP), electron cyclotron resonance (ECR)-CVD, etc. are all different methods to develop high-density plasma at low power, pressure and temperature, and to facilitate crystallization, maintaining a superior deposition rate without any surface damage. It has also been identified that dilution in hydrogen is not an essential condition for the formation of nanocrystalline silicon; presence of atomic hydrogen at very high density in the plasma, coming from the SiH$_4$, can also promote the crystallization process in an effective way without any high temperature post annealing treatment on the films.

The parallel approach in fabricating the size-controlled nano-crystalline silicon thin films is to deposit the alternative layer of alternate Si-rich layer and Si$_3$N$_4$/SiO$_2$/SiC dielectric layer have attracted substantial attention as they provide superior control over the growth of Si-ncs which, however, proceeds essentially through high temperature post-deposition annealing. During the annealing process, crystallization in the Si-rich layer in solid-phase leads to the formation of Si-ncs and their size is controlled by the thickness of the Si-rich layer within the dielectric barriers on both sides. However, the inevitable high temperature annealing step again imposes a persistent hindrance in its successful application in thin film solar cells and also affects the other pre-deposited layers of the device. In addition, the charge carriers are being obstructed by the high dielectric barriers on both sides of the Si-rich layer. In order to minimize the
obstruction, the dielectric layers should be thin enough and the Si-ncs should be closely spaced so as to allow the overlapping of the wave-functions in between the adjacent Si-ncs which can provide better charge conduction. Regarding that, low temperature deposition of superlattice films with sub-layers of hydrogenated amorphous silicon (a-Si:H) and nano-crystalline silicon (nc-Si:H) that contains Si-ncs of size controlled by the corresponding sub-layer thickness, without post deposition annealing, could be significantly important in terms of improving the carrier transport due to lower dielectric barrier of a-Si:H sub-layer, and making device fabrication feasible at low deposition temperature.

The key requirement of a proper energy selective contact for hot carrier solar cells can be achieved by resonant tunneling of charge carriers. In addition, double barrier structures consisting of zero dimensional quantum dots in amorphous dielectric matrix can provide total energy confinement in three dimensions. In achieving energy selective contacts in silicon quantum dots (Si-QDs) some efforts have already been made with Si-QDs developed within silicon-rich silicon oxide layer sandwiched between two highly dielectric SiO₂ barriers, after high temperature post-annealing treatment. Again such approach appears unrealistic from practical application point of view.

Accordingly, the present research project deals with the synthesis of silicon nano-crystals (Si-ncs) and quantum dots (Si-QDs) embedded within a dielectric matrix (a-SiC and a-SiOₓ) and the nc-Si/a-Si:H superlattice structures, specifically through low temperature CVD processing and rf-magnetron sputtering at a comparatively low-temperature (< 400°C), compatible for device fabrication at low cost. Detailed investigations of the nano-structured materials on their structural, optical and electrical properties have been studied in view of their optimization and utilization in the fabrication of devices.
1.2 Overview of c-Si, a-Si:H, nc-Si/a-Si:H, nc-Si/a-SiC, n-type nc-Si/a-SiC, nc-Si/a-SiOx, nc-Si–QDs and Si-superlattice

1.2.1 Crystalline Silicon (c-Si)

Silicon is a group IV elemental semiconductor like carbon, which falls in the face-centered diamond lattice structural group where each atom has four nearest neighbors at the vertices of a tetrahedron as in Fig 1.1(a). Silicon, in particular,

![Face-Centre diamond lattice structure of the unit cell of crystalline silicon.](image)

forms a face-centered cubic structure with a lattice spacing of 5.430710 Å.\(^{36}\) Crystalline silicon (c-Si) has an ordered crystal structure, with each atom ideally lying in a predetermined position (Fig 1.1(b)). Considering the band structure of crystalline silicon is an indirect band gap semiconductor. The specific band structure of crystalline silicon is presented in Fig 1.2. c-Si has parabolic valence and conduction band. At Γ point of the Brillouin Zone (K=0), both the valance band and conduction band show the maxima. However, at X point along <100> direction has 6 equivalent conduction minima, so it is an indirect band gap semiconductor. The indirect band gap of the c-Si is \(~1.1\) eV. However, the band gap of c-Si depends on the different physical conditions like temperature, pressure, doping density etc. The variation of the energy gap with temperature originates from two different processes. The first one arises from the change in bond lengths with temperature and can be related to the pressure coefficient of the energy gap through the compressibility and the thermal expansion coefficient.\(^{37}\) The second contribution originates in the electron–phonon interaction. The latter
dominates at elevated temperatures ($T \approx 100$ K), decreasing the band-gap energy with temperature. The electron–phonon contribution can be calculated at different levels of sophistication. At high temperatures, theory predicts a linear energy shift of the band gap with temperature, while at low temperatures the dependence is strongly nonlinear. This behavior is reflected in the various semi-empirical analytical expressions used to fit the experimental data.

Four different analytical equations exist in the literature, which allow fitting the experimental data with three or four parameters.\textsuperscript{38-41}

\begin{equation}
E_g(T) = E_g(0) - \frac{\alpha T^2}{(T + \beta)}
\end{equation}

\begin{equation}
E_g(T) = E_B - a_B \left[ 1 + \frac{2}{\exp \left( \frac{\theta}{T} \right) - 1} \right]
\end{equation}

\begin{equation}
E_g(T) = E_g(0) - \frac{\alpha T^2}{(T + \beta)}
\end{equation}

\begin{equation}
E_g(T) = E_B - \frac{\alpha \theta}{2} \left[ p \sqrt{1 + \left( \frac{2\theta}{T} \right)^p} - 1 \right]
\end{equation}
The effects of thermal expansion and the electron-phonon interaction are not explicitly considered or separately taken into account in all of the above empirical relations; therefore the physical meaning of the parameters appearing in them is not transparent. However, equation 1.1 is mostly used empirical relation for temperature dependence of band gap. The basic difference between the Eqn. 1.1 and 1.2 is in the low temperature region (<50 K): the quadratic dependence given in Eqn. 1.1 is in Eqn. 1.2 replaced by an exponential dependence and the band gap is express by Bose-Einstein expression of band gap.\(^{42}\) On the other hand, both the pressure and doping is responsible to narrow the gap with their higher value.\(^{43}\)

### 1.2.2 Amorphous Silicon (a-Si:H)

Amorphous silicon (a-Si:H) is composed of silicon atoms which are spatially arranged on a lattice that presents only short range order, no long range order exists. Compared to crystalline silicon (c-Si), the average bond angles between neighboring atoms are distorted, as schematically shown in Fig. 1.3. This leads to charge carrier scattering, broadening of the density of states and to an uncertainty in the wave vector of the electrons. This leads to massive changes in the electrical and optical properties of the material. Unsaturated valences (dangling bonds) cause energy states within the band gap leading to material with bad semiconducting properties. Saturation of the dangling bonds with hydrogen reduces this defect density and makes the material suitable for semiconductor devices. This material is then called hydrogenated amorphous silicon (a-Si:H).

A sketch of the density of states in amorphous silicon is shown in Fig 1.4. The structural disorder leads to the formation of localized "band tail" states. However, the rough classification in valence- and conduction-band still holds in a-Si:H. The bond distortion results in band tails near the valence and conduction bands: in these band tails, the electrons (or holes) wave functions are spatially localized and do not participate directly in the electronic transport.\(^{44}\) The (non-passivated) dangling bonds create deep, highly localized, electronic states near the middle of the band gap. These defects, that acts as the main recombination centers in a-Si:H, can either be positively charged (i.e. unoccupied, \(D^+\)), neutral (i.e. occupied by one electron, \(D^0\))
or negatively charged (i.e. occupied by two electrons, D\(^{-}\)). The dangling bonds act as recombination centres for the free electrons and holes, and lead to two recombination paths: one over D\(^{0}/D^{-}\) and one over D\(^{+}/D^{0}\). Since these states are localized between the valence and the conduction band it is difficult to define the optical band gap in a-Si:H. Instead the concept of a mobility gap is used, due to the localized nature of the tail states, the mobility of charge carriers sharply drops several orders of magnitude. This mobility gap is significantly higher (~1.7 eV) than the band gap of crystalline silicon (~1.1 eV).

Fig. 1.3 Lattice of hydrogenated amorphous silicon, with Si–Si and Si–H bonds, as well as dangling bonds.

Fig. 1.4 Density of states N(E) for intrinsic a-Si:H. Within the mobility band gap (delimited by \(E_C\) and \(E_V\)), the states are localized (dangling bonds and band tails).
1.2.3 Nano-crystalline Silicon in amorphous silicon (nc-Si/a-Si:H)

Nanocrystalline silicon (nc-Si/a-Si:H) will be used as a general term for a material which is a composition of crystalline grains, amorphous phase and voids, where the grain size is in the range of few micrometer to nanometer. Hydrogen saturates dangling bonds which occur at the grain boundaries and in the amorphous phase. Correspondingly, the material is called hydrogenated nanocrystalline silicon (nc-Si/a-Si:H). The actual structure of the material depends strongly on the deposition conditions and has a strong impact on the device performance.

A structural model of nc-Si/a-Si:H material is schematically shown in Fig. 1.5. From the left to the right hand side of this Fig the deposition conditions change from a highly crystalline to a predominantly amorphous growth regime. In the highly crystalline growth regime the crystalline growth originates from nucleation centers near the substrate. At increasing distance to the substrate the diameter of the crystallites increases resulting in a conical shape. The space between the crystalline grains can be filled with amorphous silicon and/or voids, depending on the deposition conditions and the substrate (see \cite{46, 47} and references therein). This growth region is called the incubation zone.

At a certain stage, equally fast growing crystalline columns with stable grain boundaries are formed. In this steady-stage of growth, characteristic properties like grain sizes and phase composition are independent of the film thickness, and disordered network is only present at grain boundaries between the crystalline columns. The
diameter of the crystalline grains depends thereby on the deposition regime (i.e. combination of silane concentration, deposition pressure, plasma power, substrate temperature etc.). The structure of the silicon inside these columns is not monocrystalline. It exhibits a high density of twin defects and stacking faults.\textsuperscript{45, 48}

Under highly crystalline growth conditions the presence of voids is especially emphasized. For this reason, the material obtained in this regime can be considered as porous.\textsuperscript{46, 48} These voids occur especially in the nucleation zone near the substrate and along the boundaries of the large diameter grains. Approaching the transition to amorphous growth, the most significant effect is a reduction of the column diameter, while extended disordered phase is only incorporated in the nucleation layer. Further adjustment of the deposition conditions in direction of amorphous growth leads to the occurrence of films with predominantly amorphous structure. Interruptions of the columns in growth direction occur, which reduces the crystallites to smaller size crystallites embedded within the amorphous matrix. Such material does not represent standard a-Si:H used e.g. for solar cells, but is a transition material between amorphous and microcrystalline silicon.

At the transition between microcrystalline (μc-Si:H) and amorphous growth the material properties change significantly. Microcrystalline silicon is in many aspects comparable to mono-crystalline silicon (c-Si). In those cases, the optical band gap and absorption coefficient $\alpha$ are very similar. Only at high photon energies $\alpha$ is significantly higher than for c-Si. This can partly be attributed to the high $\alpha$ of the amorphous phase contained in μc-Si:H (see Fig. 1.6).

![Absorption coefficient $\alpha$ vs. energy for a-Si:H/μc-Si:H and crystalline silicon (c-Si).](image)

Fig. 1.6 Absorption coefficient $\alpha$ vs. energy for a-Si:H/μc-Si:H and crystalline silicon (c-Si).
Recently, self-assembled and continuously grown nano-crystalline silicon embedded in a dielectric matrix (nc-Si/a-SiC) has attracted a great deal of interest and has been a subject of intense scientific activities, owing to their immensely promising applications in the third generation photovoltaic solar cells. The third-generation all-Si tandem photovoltaic solar cells, which rely on the quantum confinement effects coming out of the silicon nano-crystals (Si-nc), are expected to overcome the Shockley–Queisser limit of conventional solar cells and reach the high-energy conversion efficiency of 47.5% using three-cell tandem stacks. Most publications to date have focused on the preparation of Si-nc embedded in amorphous SiO$_x$ or SiN$_x$ matrices. Compared with the Si-nc embedded in a SiO$_x$ or SiN$_x$ matrices, the Si-nc embedded in an amorphous SiC(a-SiC) matrix have several striking advantages considering the fact that the barrier height of SiC (~2.5 eV) is significantly lower than that of SiO$_2$ (~9 eV) or Si$_3$N$_4$ (~5.3 eV). The low barrier of the SiC matrix is very favorable for the charge carrier transport when applied in the devices. This is because the tunneling probability of the carriers between the adjacent Si-nc in the SiC matrix can be exponentially increased, and the radiative electron–hole recombination rates can be significantly enhanced due to the strong overlap of electron–hole wave functions.

In view of further development of amorphous silicon solar cells first introduced by Carlson and Wronski in 1976, up-gradation of the window layer materials property has become one of the key issues among several others. The window layer for $p$-$i$-$n$ solar cell is always being expected with high optical band gap and good electrical conductivity so as to allow more light entering into the $i$-layer and simultaneously provide better conduction path to the charge carriers. Due to high doping efficiency and band gap, a-SiC has been extensively studied for suitable application in window layer. However, due to the amorphous matrix, the conductivity values are not high before doping. Nanocrystalline silicon (nc-Si) embedded in the amorphous silicon carbide (a-SiC) matrix could be the desired material due to its high band gap (controlled by carbon concentration and size of nanocrystals) and relatively high conductivity (contributed by the overall crystallinity). In addition, the growth of $\mu$c/nc-Si:H absorber layer is dominantly controlled by the nature of the substrate due to the lattice mismatch factor. Accordingly, the growth of nc-Si $i$-layer is being stimulated when deposited on nanocrystalline window layer in superstrate configuration. The $n/p$-a-SiC:H layer, as the
substrate, usually hinders the crystallization process while the micro/nano crystalline silicon \( p \)-layer can deliver more nucleation sites of the crystallites for the intrinsic layer.

### 1.2.5 n-type Nano-crystalline Silicon in amorphous Silicon Carbide (\( n \)-type nc-Si/a-SiC)

It has been well established that a-Si:H solar cells need an illumination through the \( p \)-type side in order to get optimum stabilized performance. This is partially caused by the fact that the hole drift mobility (HDM) in a-Si:H films is two to three orders of magnitudes lower than the electron mobility. However, nearly identical quantum efficiency QE curves were obtained for \( \mu \)c-Si:H solar cells under \( p \)- and \( n \)-side illuminations, showing a symmetrical photocurrent collection. There have been considerable data in the literature in recent years showing a difference in the open circuit voltages (\( V_{oc} \)) between \( p-i-n \) and \( n-i-p \) type amorphous silicon (a-Si:H) solar cells. Explanations for differences in \( V_{oc} \) have included effects which depend on whether the illumination comes through the \( n^+ \) or \( p^+ \) layer such as the Dember effect of land self-field. Other explanations are based on differences in the device structure, such as dopant trailing into the intrinsic layer or structural differences in the layers depending on whether they were grown on the metal substrate or on a previous a-Si layer. However, when one compares the photovoltaic properties of these two type cells, it is recognized that the open circuit voltage \( V_{oc} \) for an \( n-i-p \) type cell is usually higher by 0.1-0.2 V than that of a \( p-i-n \) type cell although almost the same values are reported for the short circuit current and for the fill factor. The high HDM and the high transparency of the Si-QD/a-SiC films layers offer a high potential for an application of the Si-QD/a-SiC films window layers in \( n-i-p \) \( \mu \)c-Si:H solar cells.

### 1.2.6 Nano-crystalline Silicon in amorphous Silicon Oxide (nc-Si/a-SiO\(_x\))

Nano-crystalline silicon in amorphous silicon oxide (nc-Si/a-SiO\(_x\)) has the similar structure like nano-crystalline silicon in amorphous silicon (nc-Si/a-Si:H) where the nano-crystalline silicon grains is embedded in the a-SiO\(_x\) matrix instead of a-Si:H matrix. The effect of oxygen incorporation in the Si-network will increase the optical transmission maintaining the higher conductivity with higher carrier mobility of the nano-crystalline silicon compared to silicon oxide or amorphous silicon which eventually make it more attractive for the window layer and also at the tunnel junction in a-Si based solar cells.
Double barrier structures consisting of Si-nc in a highly dielectric matrix are a potential candidate for energy selective contacts in hot carrier solar cell, with QDs providing a discrete energy level between two insulating barriers. In this regard, Si-nc embedded in oxygen rich SiO$_x$ ($x \approx 2$) can provide better confinement effect due to the higher band gap difference in the Si-nc ($\sim 1.1$ eV) and SiO$_x$ ($\sim 9$ eV). This is expected to give conduction of carriers strongly peaked at the discrete energy levels of Si-nc, and lower at other energies. Such a structure should exhibit negative differential resistance (NDR) characteristics in DC I–V measurement. The use of Si-nc is also advantageous since they offer total energy selection rather than confinement in one dimension such as by quantum wells. However, the fabrication of quantum dots of uniform size, for the better selectivity of hot carriers, is very challenging. For practical hot carrier solar cell it is also necessary to be able to tune the resonance energy in order to optimize the carrier collection. This may be achieved by controlling the size of the quantum dots in which discrete energy is modified due to quantum confinement in the nano-crystalline silicon.

### 1.2.7 Nano-crystalline Silicon Quantum Dots (nc-Si–QDs)

A quantum dot (QD) is a nanocrystal made of semiconductor materials that is small enough to exhibit quantum mechanical properties. Specifically, its excitons are confined in all three spatial dimensions. The electronic properties of these materials are intermediate between those of bulk semiconductors and of discrete molecules. In a semiconductor crystallite whose radius is smaller than the size of its exciton Bohr radius, the excitons are squeezed, leading to quantum confinement. The energy levels can then be modeled using the particle in a box model in which the energy of different states is dependent on the length of the box. Quantum dots are said to be in the 'weak confinement regime' if their radii are of the order of the exciton Bohr radius; quantum dots are said to be in the 'strong confinement regime' if their radii are smaller than the exciton Bohr radius. If the size of the quantum dot is small enough, the quantum confinement effect dominates (typically less than 5 nm for crystalline silicon) in which the electronic and optical properties (in particular the optical band gap) are highly tunable.

Due to indirect nature of band gap of c-Si, the electronic structure of silicon prevents this material from being a strong light emitter. In indirect band gap semiconductors like silicon, there is a mismatch in momentum space between the
electron and hole states. To conserve momentum, excitation and relaxation between the conduction band and valence band extrema require the assistance of a crystal lattice vibration. Radiative recombination of excited charge carriers is therefore a three-body process, and, as a result, it is much less efficient than the analogous two-body recombination in a direct band gap semiconductor, where the conduction and valence band extrema are matched in momentum space. The low probability of radiative recombination in indirect band gap materials favors non-radiative decay processes, and excited electrons generally lose energy as heat, not emitted photons. These materials exhibit only very faint luminescence, even at low temperatures, and this weakness has traditionally prevented the desirable extension of silicon microelectronics to silicon optoelectronics; LEDs and lasers cannot be produced from bulk silicon. These limitations can be overcome through quantum confinement of carriers within crystalline structures grown on a nanometer scale.

A simple notion of the development of the band structure of the semiconductor materials can be gained from applying the concepts of quantum mechanics and Pauli Exclusion Principle to a system of electrons interacting in a periodic potential of a crystalline lattice. The density of allowable energy states for the charge carriers of a material is given by

$$g(E) = \frac{dN}{dE}$$

where $N$ is the number of allowed states at energy level $E$. The density of states is a function of the size and dimensionality of the system. It is the ability to exploit this reduced dimensionality that encourages the study of quantum-confined materials.

A bulk or conventional three dimensional materials has a density of energy states as

$$g(E) = \frac{(2mr)^{3/2}}{2\pi^2\hbar^3}E^{1/2}$$

where $m$ is the mass of an electron and $E$ is the energy of a carrier.

This continuous range of allowable states begins to change with reduced dimensionality, as shown in Fig 1.7(b). Confining a system in one dimension, that is,
making one dimension small on the scale of the carrier wave functions produces a two
dimensional material or quantum well. For a system with well thickness $d$, the system
has a density of states given by,

$$ g(E) = \frac{m}{\pi \hbar^2 d} $$  \hspace{1cm} (1.7)

This leads to a step function defined at each allowed energy level of the system.

Confining the system again in another dimension produces a one dimensional material
or quantum wire, whose density of states is shown in Fig1.7(c), and can be expressed as

$$ g(E) = \frac{1}{d_1 d_2} \left( \frac{m^{1/2}}{\sqrt{2\pi\hbar}} \right) \sqrt{\frac{E}{\hbar}} $$ \hspace{1cm} (1.8)

where $d_1$ and $d_2$ are the confined dimensions of the wire.
Finally, confining a material in three dimensions results in a quantum box or quantum dot, whose density of states is shown in Fig 1.7(d), and is given by

\[ g(E) = \delta(E) \]  

(1.9)

The allowed energy levels are discrete and well separated, and the density of states is a series of delta functions. The discrete nature of the density of states makes the quantum dots system very similar to a molecular system in that the bands of allowed energies characteristic of a solid semiconductor have been totally lost.

This discrete density of states modifies a semiconductor’s properties so that even in a material like silicon which by nature indirect band gap, photonic applications become possible. First of all, quantum confined silicon can become a stronger absorber of light. In this discrete system, all the concepts of indirect versus direct are no longer applicable. Also, the discrete nature of the states means that all of the oscillator strength of the material is focused to transitions that match the levels. The quantum confined silicon then can become a strong absorber at exceedingly narrow resonant line widths. Sharpening of absorption lines relative to bulk behavior has been demonstrated in quantum dots synthesized from II-VI semiconductors, such as Cadmium Selenide (CdSe).

Again, the levels themselves have a finite capacity depending on the size of the system, so that only a limited number of carriers can fit into each. This enables the possibility of saturating the levels by filling them completely with excited carriers. Then absorption of energy by the system into those levels becomes impossible, and the material becomes transparent at that excitation energy (or wavelength of light). This saturable absorption is the basis of the photonic switch.

Quantum confinement has also the effect of increasing the band gap of a material relative to the bulk value. Therefore, silicon nanocrystals emit in the near-infrared to visible range. In these systems, the emission of a photon upon the radiative recombination of quantum-confined excitons occurs at an energy that depends on the nanocrystal size, and the photoluminescence is size-tunable. An analytical model, introduced by Brus in 1986, predicts that the quantum confinement effect in nanocrystals scales with confinement radius, \( r \). Neglecting higher-order terms, and the expected energy-size relationship in the simple reduced mass picture is \( 55 \)
\[ E_{g,nc}(r) = E_{g,\text{bulk}} + \frac{\hbar^2 \pi^2}{2m_{\text{red}}} r^{-2} - \frac{1.8 e^2}{4\pi \epsilon_0 \epsilon} r^{-1} \] (1.10)

Here, \( E_{g,nc}(r) \) is the band gap of the nanocrystal, which increases from the bulk value, \( E_{g,\text{bulk}} \) (1.11 eV for silicon), as \( r \) decreases. The relative dielectric constant is given by \( \epsilon \), and the reduced mass is \( m_{\text{red}} = (1/m_e + 1/m_h)^{-1} \), where \( m_e \) and \( m_h \) are the electron and hole effective masses, respectively. The dominant second term in Eqn. 1.10 is the localization energy, which scales as \( r^{-2} \), and the less important third term scales as \( r^{-1} \) to account for the shielded Coulomb interaction between electron and hole. For decreasing \( r \) (smaller dots), this term can become negligible and the energy gap varies inversely as the square of the particle radius.

The effects of quantum confinement are not seen in semiconductor systems until the particle sizes are reduced to the nanometer scale. Roughly, quantum confinement effects are expected to be seen in nanostructures when the crystallite size approximates the Bohr exciton radius for the given material. This is given by

\[ r = \frac{4\pi \hbar^2 \epsilon}{e^2 m_r} \] (1.11)

Where \( m_r \) is the reduced mass of the electron and hole pair and \( e \) is the charge on carrier. In silicon, this radius has been calculated as ~5 nm. As particle diameter reaches this small size, the electron and hole wave functions that make up an exciton are compressed closer together than in bulk systems. This confinement of the wave functions results in the energy gap increase and enhanced overlaps that are responsible for efficient visible light emission predicted from silicon nanostructures.

The quantum confinement of carriers within quantum dots or semiconductor nanocrystallites is predicted to improve the emission efficiency. Similar to the case described above for impurities in silicon, the small structures and their surfaces disrupt the symmetry of the crystalline lattice, resulting in a breakdown of the momentum selection rules in these systems. As size decreases the wave function overlap between electrons and holes increases, and makes radiative transitions more likely for structurally perfect nanocrystallites. This leads to efficient emission that is required for silicon based light emitting applications.
1.2.8 Silicon nanocrystals in superlattice structures

Superlattice is a periodic structure of layers of two or more materials. Typically the width of layers is orders of magnitude larger than the lattice constant, and is limited by the growth of the structure. As shown in the Fig. 1.8 below, it is a superlattice formed by alternating silicon rich silicon oxide (SRO) and SiO$_2$ layers, as they have the similar lattice constant and different band gap.

![Illustration of the superlattice consisting of alternating layers of silicon rich silicon oxide (SRO) and SiO$_2$ with corresponding valence band structure.]

Fig. 1.8 Illustration of the superlattice consisting of alternating layers of silicon rich silicon oxide (SRO) and SiO$_2$ with corresponding valence band structure.

Usually there are two different ways of forming superlattice structure: periodic variation of donor or acceptor impurities, periodic variation of alloy composition introduced during the crystal growth. In the first method, the electrons and holes are confined in different locations, thus reducing the recombination possibility. However, this method has large thermal diffusion of impurities, so it is hard to maintain the periodic potential profile. So the second method is more popular. It is worthy to make a difference between superlattice and multiple quantum well because they are very similar in their structure except that unlike the multiple quantum well, the superlattice barrier width is small enough that the different quantum wells are coupled with each other. In contrast, the quantum wells in multiple quantum well structure are highly
localized. This difference will result in the difference in their carrier conduction mechanisms.

In term of quantum mechanical approach, the Schrödinger’s equation for the superlattice structure can be solved using the square potential well and applying the Kronig-Penney model on it, which is very much similar to the problem related to the lattice structure. The solutions suggest discrete energy bands separated by the forbidden bands just as the conventional crystal structure energy band. But the difference of superlattice and conventional crystal is that it is a man-made material that the energy band could be well controlled by the selected layers and with of different layers.

Random arrays of silicon quantum dots embedded in a silicon oxide, nitride or carbide matrix have been studied for photovoltaic applications in the recent past. However due to the spatial disorder of the formed embedded dots, along with low control over quantum dot size and inter-dot distance, limited electrical characteristics have been reported. In order to enhance nanoscale geometrical control, the focus has consequently shifted to ‘superlattices’ formed with alternating bilayers of silicon-rich oxide (SRO) and SiO$_2$. From experiments on microelectronic devices including layers of oxide material on silicon, one can consider that the inter-dot distance, i.e. the SiO$_2$ barrier, needs to be in the range of 1–2 nm to successfully allow tunnelling conduction between neighboring dots. Such precisely controlled distances and subsequently improved conductivity have so far been possible only in the case of multilayer stacks, which involve multiple deposition steps. In order to get suitable absorber layer in multi-junction solar cell, the alternately H$_2$-diluted $i$-$nc$-$Si$:H multilayers wider optical band gap with the low degradation of the solar cells compared with $i$-$a$-$Si$:H absorber layer. In another approach, phosphorus-doped Si QD superlattice has been prepared as an active layer on a crystalline silicon substrate as a hetero-structure solar cell by alternate deposition of a SiO$_2$ layer and a SiO$_x$ layer, using Si, SiO$_2$ and P$_2$O$_5$ as the targets in an RF-magnetron sputtering system.

In a theoretical approach, a nano-chain is treated as a one-dimensional superlattice of quantum dots (QDs) of Si cores. SiO$_2$ layers between two adjoining QDs act as potential barriers. Electrons tunnel through QDs one by one sequentially under an external bias. Negative differential resistance (NDR) is found if the tunneling current through each barrier displays a NDR individually. Importantly, it has been observed that when the number of QDs increases, the peak-to-valley ratio of the NDR of the
whole structure becomes larger. This result explains well the recent I-V experiment on a SRO/SiO₂ superlattice structure and will also be useful for future device design for energy selective contacts in hot carrier solar cells. Double barrier structures consisting of a single layer of Si-QDs in SiO₂ matrix have been studied for energy selective contacts. These structures were grown with rf magnetron sputtering using Si and quartz targets followed by high temperature annealing. The formation of quantum dots has been confirmed by transmission electron microscopy. I–V measurements have shown an evidence of NDR, which is a characteristic of resonant tunnelling, with some repeatability. However, the NDR peak is very broad suggesting poor energy selectivity.

### 1.3 Outline of the Thesis

The aim in this thesis is to fabricate silicon nano-crystals (Si-ncs) and quantum dots (Si-QDs) dispersed within a dielectric matrix of a-SiC and a-SiOₓ and in the nc-Si/a-Si:H superlattice structures, specifically through low temperature chemical vapor deposition processing and rf-magnetron sputtering at a comparatively low-temperature, well-suited for low cost device fabrication. Comprehensive investigations of these nano-structured thin films on their structural, optical and electrical properties have been studied in view of their optimization and application in the assembly of devices.

Chapter 2 describes the various techniques used in thin film deposition and basic physics and chemistry of the rf plasma enhanced chemical vapor deposition (both capacitively and inductively coupled) and rf magnetron sputtering process which we have utilized for the deposition of nano-structured thin films.

Chapter 3 concentrates on the different measurement tools for the characterization of the structural, optical and electrical properties of the various silicon thin films, in details.

Chapter 4 focuses on the tuning of the size of the Si-nc by the thickness of nc-Si:H sub-layer (t_{nc}) in the a-Si:H/nc-Si:H superlattice thin films and the effect of the Si-nc size on the optical and electrical transport properties have been extensively investigated. The high absorption coefficient at higher energy, wide optical gap due to the quantum confinement effect arising from the Si-nc and the charge conduction by Poole-Frenkel mechanism will promote these a-Si:H/nc-Si:H superlattice thin films as
the potential candidate for the different $i$-layer in the tandem structured all silicon solar cells.

Chapter 5 deals with the development of thin films of doped nano-crystalline silicon embedded in amorphous silicon carbide in inductively coupled plasma assisted chemical vapour deposition unit ($\text{SiH}_4+\text{CH}_4$)-plasma with or without hydrogen dilution at low substrate temperature, wherein Si–C bonds in an amorphous matrix would widen the optical band gap and the embedded high density tiny Si-nc of mostly $<220>$ crystallographic orientation provide high electrical conductivity as well as an enhanced optical band gap due to quantum size effect. The wide optical gap and superior electrical conductivity would be used as window layer in $n$-$i$-$p$ solar cells while high deposition rate will provide low-cost fabrication. The reported room temperature dark conductivity at wider band gap has been found to be much higher compared with the present literature reports.

Chapter 6 concentrates on thin films of Si-QD/a-$\text{SiO}_x$ which has been achieved at a low temperature $\sim$400°C, from one step process by reactive rf magnetron co-sputtering of c-$\text{Si}$ wafer and pure $\text{SiO}_2$ targets, in the ($\text{H}_2+\text{Ar}$)-plasma. Formation of a double-barrier structure has been primarily identified from the X-ray reflectivity data and exclusively confirmed from the NDR-like current appearing in the $J$-$E$ characteristic curve peaks, determined by the discrete energy levels of c-$\text{Si}$ QDs, at which it could be used as energy selective contacts in hot carrier solar cells.

Finally, in Chapter 7, some general conclusions are drawn and we provide our perspective for the future of silicon quantum dots or nano-crystals embedded in amorphous dielectric matrix or in superlattice structure.
1.4 References


