CHAPTER 7

The nc-Si/a-SiN_x:H QDs thin films: an alternative material for solid-state light emitting applications

7.1 Introduction

Light emission from silicon has been identified as a topic of general scientific interest. Owing to its indirect band gap of 1.12 eV, silicon in the bulk is considered as a material of very poor optical radiative efficiency and can only produce light below the visible range. However, when silicon is in the form of low dimensional structures like, nanocrystal (nc-Si) or quantum dot (Si-QD), nanowire (Si-NW), superlattices etc., it reveals improved light emission at room temperature [1–14]. Such reports have claimed efficient photonic applications of silicon in future, where silicon-based light-emitting diodes represent promising candidates for the next generation of full-color flat panel displays, optical interconnections, telecommunications, and lasers. The advantages of silicon-based light emitting devices include complementary metal-oxide-semiconductor compatibility, system feasibility, and their low cost of fabrication. Although a variety of emission colors from porous silicon [11] and nanocrystalline silicon [15] shows a sufficiently high efficiency for applications, the
tuning of emission color, particularly in the short-wavelength region, continues to be a challenge because the silicon/dielectric interface plays an important role in the formation of radiative states [16]. In the recent past, a great deal of research on silicon nanocrystals embedded in a silicon oxide matrix has been conducted because of their potential for applications in silicon-based optoelectronic devices. However, silicon oxide as an efficient matrix material that hosts silicon nanostructures has limitations in device fabrication because of several reasons reported in the literature [16,17]. Nanocrystalline silicon embedded in hydrogenated amorphous silicon-nitride matrix (nc-Si/a-SiNₓ:H) is currently attracting much attention as a candidate for efficient light emitting devices [2,9,10] wherein the matrix silicon-nitride (SiNₓ) plays an important role because of its lower tunneling barrier and higher dielectric constant.

In this chapter, a tunable wide range (1.67-3.02 eV) visible photoluminescence is being demonstrated from inductively coupled plasma synthesized nc-Si/a-SiNₓ:H QDs thin films by varying the deposition pressure in a narrow range at low substrate temperature ~250 °C. A comprehensive correlation between photoluminescence (PL) and structural properties has been done from which quantum confinement effect (QCE) has been assigned to be mostly responsible for the light emission.

### 7.2 Experimental Section

#### 7.2.1 Material Synthesis

Inductively Coupled Plasma-CVD technique in radio frequency (13.56 MHz) low-pressure plasma was employed to prepare silicon-nitride films on p-type (100) silicon substrate, Corning® Eagle2000™ glass and carbon coated copper microscope grids. A mixture of silane (SiH₄), ammonia (NH₃), and hydrogen (H₂) were used as reactant gas sources, maintaining a flow rate ratio SiH₄ : NH₃ : H₂ = 2 sccm : 0.6 sccm : 38 sccm. The substrate temperature during deposition was fixed at 250 °C, while the chamber pressure was varied from 10 to 50 mTorr. No post-annealing process was employed after growing the silicon nitride films.

#### 7.2.2 Characterizations of the Material

Thickness of the films was determined by a Dektak 6M stylus profiler. For uniform comparison, thickness of all the films was maintained at ~4000 Å. The room
temperature PL spectra were obtained using a He-Cd laser source, with a uniform excitation of 325 nm. The luminescence spectrum was monitored using a TRIAX 320 monochromator fitted with a cooled Hamamatsu R928 photomultiplier detector. The Raman spectra were obtained by Renishaw inVia Micro-Raman spectrophotometer (Serial No. 12W143) at room temperature in a backscattering geometry, using 514 nm Ar⁺ Laser as the excitation source, at a power density of 2 mW/cm². High-resolution transmission electron micrographs (HR-TEM) as well as selected-area electron diffraction (SAED) patterns were obtained on ~30 nm thick samples deposited on carbon coated copper microscope grids supplied by Pacific Grid-Tech, USA, using a JEOL-JSM2010 transmission electron microscope operating at 200 kV. To observe the surface morphology, Veeco (di CP-II) atomic force microscope (AFM; Bruker AXS, Mannheim, Germany) has been used. The optical absorption and reflection measurements in the UV–visible region at room temperature were performed using a double beam spectrophotometer (Hitachi 330, Japan). The silicon–hydrogen–nitrogen bonding structure of the films was investigated from the infrared vibrational spectra obtained by a Nicolet Magna-IR 750 FTIR spectrometer. Electrical conductivity of the samples was measured with coplanar Al electrodes deposited by thermal evaporation at room temperature, and the measurement was carried out in vacuum of ~10⁻⁶ Torr, using a Keithley 6517A electrometer, after annealing the samples at 450 K for 1 h. The evacuation and the thermal annealing process were adopted to eliminate the effects of adsorbed gases, moisture and light induced degradation, if any.

7.3 Results

Fig. 7.1 shows the photoluminescence (PL) spectra of nc-Si/a-SiNx:H QDs thin films deposited by inductively coupled plasma at different pressure, p, varying from 10 to 50 mTorr. All these samples showed intense photoluminescence (PL) of individual color in the visible range. With the increase of pressure the PL peak energy has been found to be blue-shifted. The PL spectra for sample p10 and p20 contain two prominent peaks in the near visible region, whereas, the remaining samples (p30, p40 and p50) show single peak photoluminescence at higher energies. The relative intensity ratio of the lower energy peak of the sample p10 and p20 decreases with the increase of pressure and finally it diminishes from the PL spectrum of sample p30. The PL peak energy shifts from ~1.67 to 3.02 eV and the PL peak intensity (height)
increases systematically with increasing chamber pressure from 10 to 50 mTorr, as shown in Fig. 7.1. On varying the substrate temperature between 400–150 °C we have previously reported photoluminescence from nc-Si/a-SiNₓ:H thin films over the energy range 1.66–2.47 eV [9]. The wider variation of PL peak energy (~1.67–3.02 eV) with chamber pressure in the present work is very much promising for its effective application into light emitting devices. All the individual PL spectrum are not being found as symmetric, however, the shape of the two most high energy spectrum (sample p40 and p50) could be considered as roughly symmetric Gaussian. Deconvolution of the remaining three, corresponding to the sample p10, p20 and p30, might be helpful in order to finding the different origins of photoluminescence.

The optical density data of the samples prepared at different pressure was obtained from the absorbance and reflectance spectra of the films in the UV–vis region. The optical gap ($E_g$) was estimated from the Tauc’s plot [18] and its variation with pressure, $p$ is shown in Fig. 7.2. The gradual widening of optical gap of the hetero-structure in the range 2.02–3.05 eV is being considered as a result of band gap engineering in the material by plasma processing and the large variation of the absorption gap has been observed by varying only the pressure within a narrow range, 10–50 mTorr.

**Figure 7.1:** Room temperature photoluminescence (PL) spectra, under 325 nm excitation by He-Cd laser, of nc-Si/a-SiNₓ:H QDs thin films deposited by ICP-CVD at different pressures, $p$, varying from 10 to 50 mTorr.
CHAPTER 7  The nc-Si/a-SiN\textsubscript{x}:H QDs thin films: an alternative material for solid-state light emitting applications

Figure 7.2: Variation of optical (Tauc) gap, $E_g$, for nc-Si/a-SiN\textsubscript{x}:H QDs thin films as a function of deposition pressure, $p$.

Fig. 7.3(a) represents the typical low magnification HR-TEM image of the sample prepared at $p = 40$ mTorr that identifies a homogeneous distribution of nanocrystalline silicon quantum dots (nc-Si QDs) within the amorphous silicon nitride matrix. Fig. 7.3(b) represents the magnified view of single QD, which is spherical in shape and the crystal planes are noticeable within it. In general, quantum dots are denser material and relatively dark in appearance, randomly distributed within a less dense matrix, here a-SiN\textsubscript{x}:H. The bright diffuse rings with absence of spots in the selected area electron diffraction (SAED) pattern (Fig. 7.3(c)) indicate the existence of tiny crystalline grains with two prominent orientations, $<111>$ and $<220>$, having interplaner spacing 0.313 nm, and 0.198 nm, respectively; while the less prominent ring represents $<311>$ orientation with interplaner spacing 0.165 nm. The average diameter of the well separated nanocrystalline silicon quantum dots (nc-Si QDs) was estimated as $\sim2.7$ nm for the sample p40 with a number density of $\sim1.2\times10^{12}$ cm$^{-2}$.

The surface morphology and roughness of the deposited films were studied using atomic force Microscope (AFM) and the corresponding 2D topographic images for the films prepared at $p = 20$ and 40 mTorr are shown in Fig. 7.4. Both the surfaces contain clusters, very few isolated grains, and pits; however, the voids are not clearly visible in the surfaces, providing an overall good packing of the networks. The average cluster size seems to reduce on increasing pressure providing smaller surface
Figure 7.3: (a) Low magnification HR-TEM micrograph of the nc-Si/a-Si\textsubscript{N\textsubscript{x}}:H QDs films prepared at $p = 40$ mTorr, (b) corresponds to high magnification image of a single Si quantum dot (QD) and (c) represents the corresponding SAED pattern, demonstrating three different rings of increasing diameter, concerning (111), (220) and (311) c-Si planes, respectively.

roughness. The root mean square surface roughness ($\delta$), as estimated from the statistical analysis of AFM images, has been found to reduce from 3.5 to 2.2 nm when pressure increases from 20 to 40 mTorr.

Figure 7.4: 2D AFM images of the films p20 and p40, prepared at deposition pressure, $p = 20$ and 40 mTorr, respectively. The length scale of both the images is in the unit of $\mu$m (i.e. area is 4$\mu$m x 4$\mu$m).
CHAPTER 7  The nc-Si/a-SiN\textsubscript{x}:H QDs thin films: an alternative material for solid-state light emitting applications

Figure 7.5: 3D view of the first order Raman spectra for different \( p \). Red shifting of peak frequency and widening of Raman band have been directed by arrow. Inset presents deconvolution of the first order Raman spectrum corresponding to sample p10, into three satellite components.

First order Raman spectra of the samples deposited at different \( p \) have been displayed in Fig. 7.5. With increase of \( p \) from 10 to 50 mTorr, a continuous red shift of peak frequency associated with asymmetric broadening in the line shape was identified, attributing modification in the nature of the network structure with simultaneous reduction in size of the crystalline grains. The quantitative estimation of the crystalline volume fraction in each sample was performed from Raman spectra by deconvolution of each spectrum into three Gaussian components corresponding to nanocrystalline (nc-Si), amorphous (a-Si) and the intermediate ultra-nanocrystalline (unc-Si) component and the typical deconvolution corresponding to the sample p10 has been shown in the inset of Fig. 7.5. The volume fractions of the individual components were estimated and the total crystalline volume fraction (\( X_C \)) was obtained as: \( X_C = X_{nc} + X_{unc} \) [18]. The variations of \( X_C \) and \( X_{unc} \) with pressure are given in Fig. 7.6(a). The reduction in overall crystallinity (corresponding to \( X_C \) varying from 75 to 46%) along with simultaneous increase in the ultra-nanocrystalline fraction, \( X_{unc} \), from 18 to 27% identifies an exciting structural modification of the network with increasing deposition pressure, which in turn was controlled by the variation of nitrogen incorporation in the network. The enhanced magnitude of ultra-nanocrystalline component indicates the favored growth of tiny crystallites with increasing pressure.
Figure 7.6: (a) Variations of the crystalline ($X_C$) and ultra-nanocrystalline volume fraction ($X_{unc}$) with deposition pressure, $p$. (b) Variations of the size of nc-Si QDs estimated from first order Raman spectra with $p$.

In addition, the consecutive blue shift of the PL band can be correlated with the red shift of TO crystalline Raman peak identifying continuous size reduction of the nanocrystallites on increasing pressure. The nanocrystalline peak position was observed at ~514.63 cm$^{-1}$ for the sample deposited at $p = 10$ mTorr, whereas, it shifted to ~511.35 for the sample at $p = 50$ mTorr.

The average grain size has been estimated from Raman spectrum using the relation [18]

$$\left[\omega_L - \omega_0\right]^2 + \left(\frac{\Gamma_0}{2}\right)^2 \approx \frac{1}{3L} \cdot \exp\left(-\pi^2\right)$$

(7.1)

where $\omega_L$ is the frequency of the crystalline like mode for a nanocrystal of size $L$. The $\omega_0$ and $\Gamma_0$ are 520 and 3.5 cm$^{-1}$, respectively, for crystalline silicon. In our previous
works, a comparison between the estimated size from XRD, HR-TEM and Raman using \textbf{Eq. (7.1)} was reported and in all cases a close proximity in grain sizes estimated from above mentioned three different processes was observed that established the general acceptance of the formula [in \textbf{Eq. (7.1)}] for finding out the grain size from Raman spectra [18,19]. The size of nc-Si QDs decreases from \textasciitilde5.4 \text{ nm} at \textit{p} = 10 \text{ mTorr} to \textasciitilde2.2 \text{ nm} at \textit{p} = 50 \text{ mTorr} and its nature of variation has been shown in Fig. 7.6(b).

\textbf{Fig. 7.7(a)} shows the typical FTIR spectrum of the film prepared at \textit{p} = 30 mTorr, where the characteristic features of silicon nitride, notably the Si–N symmetric and asymmetric stretching mode at \textasciitilde480 and \textasciitilde850 cm\textsuperscript{-1}, respectively, Si–H stretching modes at \textasciitilde2150 cm\textsuperscript{-1}, the Si–H wagging mode at 640 cm\textsuperscript{-1} and the N–H wagging/rocking mode at \textasciitilde1170 cm\textsuperscript{-1}, have been exhibited [20,21]. With the increase of the deposition pressure, the intensities of the Si–N absorption peaks increase, whereas, that of the Si–H absorption peaks decrease. The decreased intensity of Si–H wagging peak with increasing deposition pressure has been shown in the inset of \textbf{Fig. 7.7(a)}. The evolution of the Si–N asymmetric stretching absorption spectra at \textasciitilde850 cm\textsuperscript{-1} with pressure has been shown separately in \textbf{Fig. 7.7(b)}. The absorption intensity of the Si–N asymmetric stretching vibration increases monotonically with increasing \textit{p}. Beside the increased amplitude, the peak position of the Si–N asymmetric stretching peak shows a slight blue shift when \textit{p} is decreased (marked by a arrow in \textbf{Fig. 7.7(b)}). Cheng \textit{et al.} [22] considered it as an initiation of higher electro-negativity of N atoms than Si atoms in the network. The absorption coefficient of Si–H stretching mode vibration around \textasciitilde1925-2300 cm\textsuperscript{-1} has been plotted separately for the films deposited at different pressures between 10–50 mTorr, as shown in Fig. 7.7(d) which demonstrates a continuous reduction of absorption intensity with increasing \textit{p}.

The bonded nitrogen content, \(x\) in SiN\(_x\) was estimated from the Si–N asymmetric stretching mode vibration (\textasciitilde850 cm\textsuperscript{-1}), as

\begin{equation}
 x = \frac{A_\omega}{N_{Si}} \int \frac{\alpha(\omega)d\omega}{\omega}
 \end{equation}

where, the oscillator strength, \(A_\omega = 6.3 \times 10^{18} \text{ cm}^2\) and \(N_{Si} = 5 \times 10^{22} \text{ cm}^{-3}\) is the atomic density of crystalline silicon [23]. The nitrogen content increased monotonically with the increase of deposition pressure, as shown in \textbf{Fig. 7.7(c)}. At \textit{p} = 10 mTorr, the estimated \(x\) value was \textasciitilde0.18, which increased with increasing \textit{p} and attained \textasciitilde0.69 at \textit{p}
Figure 7.7: (a) Typical FTIR spectrum of nc-Si/a-SiN$_x$:H QDs films deposited at $p = 30$ mTorr. Inset presents the magnified view of the variation of Si-H wagging mode, (b) The intensity variation of Si-N asymmetric stretching absorption band, (c) Variation of bonded nitrogen content, $x$ in SiN$_x$ and hydrogen content $C_H$ (in at.%) with $p$, and (d) Absorption co-efficient spectrum of Si-H stretching band for films with different $p$. 

for $p = 50$ mTorr. The bonded hydrogen content $C_H$ (in at.%) was estimated from the absorption peaks of the Si–H wagging mode at $\sim$650 cm$^{-1}$ and N-H stretching mode at $\sim$3300 cm$^{-1}$ using the following formula:

$$C_H = \left[ \frac{A_\omega}{N_{Si}} \frac{\alpha(\omega)d\omega}{\omega} \right] \times 100\%$$ \hspace{1cm} (7.3)

where, $A_\omega = 1.6 \times 10^{19}$ cm$^{-2}$ for Si-H wagging and $2.8 \times 10^{20}$ cm$^{-2}$ for N-H stretching, $N_{Si} = 5 \times 10^{22}$ cm$^{-3}$ [24,25]. The hydrogen content decreased monotonically, opposite to the variation of nitrogen content with the increase of pressure, as demonstrated in figure (Fig. 7.7(c)). At $p = 10$ mTorr, the estimated value of $C_H$ was $\sim$9.2 at.% that gradually decreased to $\sim$3.7 at.% at $p = 50$ mTorr.

For efficient light emitting application of a material, significant electrical conductivity is always needed. Hence, it was wise to measure the electrical
conductivity simultaneously. **Fig. 7.8** presents the variation of room temperature electrical conductivity ($\sigma$) of nc-Si/a-SiNx:H QDs thin films with change in deposition pressure. At $p = 10$ mTorr $\sigma \approx 3.77 \times 10^{-3}$ S cm$^{-1}$ which is significantly high compared to the similar undoped silicon films reported in the literature [19]. Conductivity, $\sigma$ decreased gradually with the increase of $p$ and finally attained a magnitude $\approx 8 \times 10^{-6}$ S cm$^{-1}$ at $p = 50$ mTorr, where the network structure was amorphous dominated having crystallinity, $X_C \approx 46\%$.

### 7.3 Discussion

The overall shift of PL spectra towards higher energy with increasing chamber pressure could be considered as a consequence of quantum confinement effect (QCE) occurring in the nanostructured system, as the size of the Si QDs has been estimated to reduce systematically with chamber pressure (**Fig. 7.6(b)**). However, the asymmetric Gaussian nature of the PL spectra and the appearance of corresponding shoulders and additional peaks for the samples p10, p20 and p30 indicate the presence of many other origins of photoluminescence [26] to co-exist with band-to-band recombination due to QCE. Quantum confinement effect occurs when dot dimension is of the order of the Bohr radius, $r_B$ (for silicon $r_B \approx 5$ nm) of a material. In addition, radiative defects in the films could be the other origin of PL for indirect band gap material like, silicon. The
Figure 7.9: Deconvolution of PL spectra corresponding to the samples prepared at $p = 10$, 20 and 30 mTorr, into possible satellite components arising out of defect contributions and band-to-band recombination due to quantum confinement effect.
major radiative defect energy levels at 1.8, 2.4 and 3.0 eV were reported earlier for silicon-nitride films [27,28]. Besides this, oxygen related defects, inherently residing within Si-based micro- and nano-structured thin films, also play vital role in the appearance of visible luminescence from silicon nanocrystal [29]. For defect related PL the peaks should appear only near the corresponding defect energy levels. Therefore, the PL spectra with variable peak positions should mostly be attributed to the quantum size effect.

For a detailed understanding regarding the origin, the PL spectra corresponding to the samples p10, p20, and p30 have been deconvoluted into possible satellite components and those are shown in Fig. 7.9. The component (Q1) at ~1.67 eV for p10 may result from band-to-band recombination in nc-Si QDs and that appears as (Q2) at ~1.95 eV for p20 and as (Q3) at ~2.24 eV for p30 sample. The origin of the satellite band (a1) at ~1.5 eV for sample p10 is not clear to us. In one way, it may be attributed to the recombination at defect energy level, however, this band is being found to appear as (a2) at ~1.53 eV for sample p20 and this slight shift toward higher energy may rise question regarding its origin as defect states. Alternatively, the components (a1) and (a2) may be considered to originate from similar quasi direct band-to-band recombination in a separate group of Si nanocrystals of larger size, additionally present in the network. This narrow PL band becomes further narrower, less intense and blue shifted in (a2) due to the average size reduction of this group of larger size Si nanocrystals and their presence in lower density within the network for sample p20, grown at higher pressure. The (b1), (b2) and (b3) components for samples p10, p20 and p30, respectively, at ~1.8 eV can be attributed to the following recombination processes: between conduction edge of the intrinsic band and N_{4}^{+} level, and between the N_{4}^{+} and N_{2}^{0} states. It has been noted that the intensity of ~1.8 eV PL component decreased with the increase of pressure from 10–30 mTorr and diminished from the PL spectrum at 40 mTorr sample that basically indicates the presence of reduced number of defects at higher pressure.

According to effective mass theory, the energy gap, $E$, for three-dimensionally confined silicon nanocrystals can be expressed as:

$$E = E_{\text{bulk}} + Q / L^2$$

where $E_{\text{bulk}}$ is the bulk crystal silicon band gap, $L$ the dot size, and $Q$ the confinement parameter. The variation in the band gap energy ($E$, in eV) of the nc-Si/a-SiN_x:H QDs
Figure 7.10: Band gap widening on reduction in the size of nc-Si QDs. Data: (red circle) obtained from PL peak position, (blue square) obtained from Tauc’s plot and (navy line) fitted PL data using effective mass theory. Reasonably good match between data and the plot demonstrates quantum confinement phenomena to occur in the silicon-nitrogen-hydrogen heterostructure.

estimated from the associated PL peak position has been plotted in Fig. 7.10, as a function of average size (L, in nm) of the QDs. Considering the quantum confinement phenomena occurring in the silicon–nitrogen–hydrogen complex system, the least square fit plot to the data in the form of above equation leads to the semi-empirical relation:

$$E = 1.10 + \frac{12}{L^2}$$  \hspace{1cm} (7.5)

where $E_{\text{bulk}} = 1.10$ eV matches well with the literature and a reasonably high quantum confinement parameter, $Q = 12$ eV nm$^2$ have been demonstrated [4,30,31]. The widening of optical gap (Tauc gap), $E_g$, on reduction in the size of the quantum dots has also been plotted in Fig. 7.10, showing close proximity with the PL data and demonstrating similar quantum confinement effects influencing the optical gaps [32].

At higher deposition pressure the dissociation of Si–H and N–H bonds increases, resulting in enhanced silicon and nitrogen atoms having dangling bonds. The increase in dangling bond populated silicon atoms facilitates the creation of nucleation sites and the formation of silicon clusters in the silicon nitride film during the growth process. Increasing nucleation sites induce in size-reduction of the silicon clusters because of distribution of growth-precursors. Simultaneously, enhanced
nitrogenation to the network decreases the overall crystallinity of the material. High surface coverage by atomic hydrogen, contributed from high density inductively coupled plasma produced by high density of electrons \(n_0 \sim 10^{12} \text{ cm}^{-3}\) at 10 mTorr at very low pressure (in the mTorr range) helps in forming plenty of ultrananocrystallites within the amorphous nitrogenated network grown at 250 °C [33–36]. In the present deposition system the plasma is generated by a built in four-antenna low inductance flat spiral coil and the plasma is confined at the vicinity of the quartz plate of ICP source. ICP-discharges, produced by the RF power applied across a dielectric window via electromagnetic coupling, are advantageous for higher plasma density, lower plasma sheath potentials at the growth surface etc., compared to different other low-pressure plasma discharges. The growth holder is located at such a distance that the direct contact of the growth from the plasma could be avoided so that high quality film can be produced.

In general the Si-QDs have been reported to be produced through multi-step routes, the most fundamental of which is the high temperature processing as either pre-deposition or post-deposition annealing at \(~1000 \text{ °C}\) or above. As regards the fabrication and the subsequent integration of high-performance devices, a high annealing temperature is unsuitable from a technical point of view since the thermal budget is extremely high and the diffusion of dopants would be intolerably fast. Compared to various usual methods of Si-QD formation, the supremacy of plasma processing has been well established, being the most favored route compatible with even miniaturized integrated circuit design and fabrication. Using low temperature one-step and spontaneous plasma processing by CVD, we have previously reported the growth of nc-Si QDs of controlled size, density and distribution within a-Si/SiO\(_x\) matrix [4]. Regarding the growth of nc-Si QDs in a-Si\(_x\) matrix, only few reports are available in the literature [30,31]. Present work deals with the controlled growth of nc-Si QDs in a-Si\(_x\):H dielectric matrix through one-step low temperature spontaneous plasma processing, utilizing the high density low pressure inductively coupled plasma, enriched in high atomic H density and operating in a virtual remote plasma configuration.

Strong visible photoluminescence (PL), tunable over wide range (1.67–3.02 eV), from nc-Si/a-Si\(_x\):H QDs thin films having significant electrical conductivity, deposited in single step synthesis by inductively coupled plasma CVD, described in
the present work would be an appropriate candidate for fabrication of light emitting devices (LEDs). The tunability of PL response over the significantly wide range was achieved by varying the size of the nc-Si QDs from ~5.4 to 2.2 nm, obtained by controlling a single parameter, the low pressure of the plasma within a narrow range (10–50 mTorr), maintaining a notably low growth temperature (250 °C), and here lies the novelty of this work.

7.4 Conclusions

Intense visible photoluminescence tunable over a wide range (1.67–3.02 eV) has been observed from nc-Si/a-SiNₓ:H QDs thin films. Planer ICP-CVD of 13.56 MHz RF plasma was employed to prepare the films using a mixture of silane (SiH₄), ammonia (NH₃), and hydrogen (H₂) gases, by varying the deposition pressure within a narrow range (10–50 mTorr) at low substrate temperature (250 °C). The origin of the PL spectra with variable peak position was attributed mostly to the band-to-band recombination due to the quantum confinement effect (QCE) in the nanocrystalline silicon QDs of size ~Bohr radius. A large amount of atomic hydrogen flux that originates due to the high degree dissociation of the gas molecules in high-density inductively coupled plasma (ICPs), provides very high surface coverage during growth, passivate well the nonradiative dangling bonds in the Si-network and produces tiny nc-Si quantum dots demonstrating visible photoluminescence. The red-shift of Raman peak and the corresponding broadening of the Raman line due to the confinement of optical phonons, indicate the size reduction of Si QDs within amorphous dominated nature of the network, during the increase of plasma pressure. Size estimated from the Raman spectra varies from 5.4 to 2.2 nm as pressure goes from 10 to 50 mTorr. HR-TEM image of the sample gives the physical evidence of the presence of Si quantum dots (Si QDs) within the material.

The tunable photoluminescence and the widening of band gap as a consequence of quantum size effect along with significantly high electrical conductivity from nc-Si/a-SiNₓ:H QDs thin films prepared at a very low pressure, described in the present work, demonstrates enormous promise for light emitting applications such as, the fabrication full-color flat panel displays, etc.
Bibliography