3.1 Introduction

The most innovative approach in third-generation photovoltaics is to directly address the fundamental loss mechanisms in conventional solar cells in order to find ways of surpassing their inherent limiting efficiencies [1–4]. Several advances have been proposed to substantially increase the energy conversion efficiency of solar cells that includes: band gap engineering of Si based materials for all-silicon (Si) tandem cells, hot carrier cells using quantum dots, and up- and down-conversion of incident photons etc. The loss mechanism arising out of imperfect collection due to recombination close to or at the surface can be reduced by using photoluminescence, whereby higher energy photons in the UV region are shifted mostly into visible energy range where the cell has a higher spectral response. The photoluminescence signal serves as the photon converter by transforming the high energy photons into lower energy ones permitting an easier absorption by the cell matrix [5]. It has been reported
that tandem cells based on silicon nanocrystals (Si-ncs) embedded in silicon dielectrics may be possible [6,7]. Silicon-nitride is a very promising matrix material for the development of Si-ncs for its application in third generation solar cells because of its low tunneling barrier [8]. The material is transparent over a wide range of wavelengths and can be used in surface passivation and as antireflection coating. In addition, high dielectric constant of silicon-nitride provides enhanced electric field that can improve the recombination rate and finally enhance the light emission [9,10]. Consequently, silicon-nitride combined with silicon-nanocrystals that exhibit quantum size effect and demonstrates photoluminescence, is well suited for applications in solar cells and could offer improved photonic properties compared to bulk silicon for optoelectronic application as well [11–20]. Detail investigation on the structural, optical, and electrical properties of Si-ncs within silicon-nitride dielectric matrices is necessary for better understanding of the material for its proper utilization in devices.

In this chapter, a comprehensive structural investigation of low-temperature and low-pressure plasma synthesized nc-Si/a-SiNx:H has been carried out, using various spectroscopic and microscopic tools. In order to obtain a good interpretation on the usefulness of the material in solar cells, the increase of relative intensity ratio of (220) and (111) peaks \[\frac{I_{(220)}}{I_{(111)}}\] on XRD spectra has been studied, as best values of open-circuit voltage (\(V_{OC}\)) in solar cells identifies low recombination losses in (220) textures [21]. The nc-Si/a-SiNx:H films containing Si nanocrystals of average size <3 nm exhibited strong blue emission band composed of a double peak (~413 nm and ~438 nm) and two shoulders (~467 nm and ~498 nm). The rising concentration of the Si ultra-nanocrystalline and/or grain boundary component of Raman spectra has been correlated to the origin of some PL component and the relative dominance of thermodynamically preferred crystalline grains with (220) crystallographic orientation, with increasing nitrogenation of the network.

### 3.2 Experimental Details

The development of silicon-nitride nanostructures was pursued by inductively coupled plasma originated from RF (13.56 MHz) decomposition of Silane (SiH\(_4\)), Hydrogen (H\(_2\)) and Ammonia (NH\(_3\)) mixture. Other process parameters include: RF power 500 W, substrate temperature 300 °C and gas pressure 30 mTorr. P-type (100) silicon wafers and corning glass substrates were used for film deposition. Before
deposition, the wafers were etched in an HF solution to remove the surface oxide layer. This series of samples were synthesized with the variation of NH$_3$ flow rate from 0 sccm to 1.0 sccm at interval of 0.2 sccm, keeping the flow rates of SiH$_4$ and H$_2$ constant by 2.0 sccm and 38.0 sccm respectively.

The deposited films were analyzed by several characterizations, as mentioned below. Thickness of the films was determined by a Dektak 6M stylus profiler. The X-ray diffraction analysis was carried out using a conventional Cu K$_\alpha$ X-ray radiation ($\lambda=1.5418$ Å) source and a Bragg diffraction set-up (Seifert 3000P). 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/cm$^2$. Dielectric constant of the films was measured using a fixed angle of incidence spectroscopic ellipsometer (JobinYvon). This experimental setup had a xenon lamp as a light source, a polarizer, a detector, and a monochromator, which allowed optical measurement in the UV–visible range of wavelength corresponding to a span of energy from 1.5–5.0 eV. The optical density data of the samples were obtained from absorption and reflection measurements in the UV-visible region at room temperature using a double beam spectrophotometer (Hitachi 330, Japan) and the optical band gaps were estimated using Tauc’s plot. 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. To observe the surface morphology, Veeco (di CP-II) atomic force microscope (AFM; Bruker AXS, Mannheim, Germany) has been used. High-resolution transmission electron micrographs (HRTEM) as well as selected-area electron diffraction (SAED) patterns were obtained on samples ∼30 nm thick and deposited on carbon coated copper microscope grids supplied by Pacific Grid-Tech, USA by means of a JEOL-JSM2010 transmission electron microscope operating at 200 kV. 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. In order to block the appearance of second harmonic of the excitation wavelength in emission spectrum, an appropriate filter was used.
3.3 Results

3.3.1 X-Ray Diffraction Study

Fig. 3.1(a) represents the X-ray diffraction (XRD) spectra for the films prepared at different $R$, where $R$ is the ratio of ammonia (NH$_3$) to silane (SiH$_4$) flow rate in the plasma. The broadband centered at $2\Theta \sim 25^\circ$ corresponds to the amorphous silicon component. However, the peaks at $2\Theta = 28.34^\circ$, $47.17^\circ$ and $56.08^\circ$ correspond to (111), (220) and (311) crystallographic planes of silicon, respectively, and those are quite sharp as well as intense for the film prepared at $R = 0$, without ammonia. It has been identified that the intensity of the XRD peaks reduces monotonically with the increase of ammonia flow in the plasma and the (311) peak virtually disappears for the film prepared at $R = 0.5$, demonstrating gradual deviation of crystallinity of the silicon network. The average crystallite size of the silicon films has been estimated from the full width at half maximum (FWHM) of the (111) diffraction peaks using Debye-Scherrer formula and it has been found to reduce systematically from 13 nm to 2.4 nm with the increase of $R$ from 0 to 0.5, as shown in Fig. 3.1(b).

It has been noted that the XRD peaks corresponding to (111) orientation are, in general, most intense, i.e., the silicon crystallites are preferentially grown along <111> crystallographic orientation. However, careful observation reveals that the relative intensity of the (220) peak, $I_{220}/I_{111}$, gradually increases and attains an equal strength to that of (111) peak on increase in $R$ at 0.5, as shown in Fig. 3.1(b). The <111> orientation arises from random nucleation whereas, <220> due to the growth of

![Figure 3.1: (a) X-ray diffraction spectra of nc-Si/a-Si$_x$N$_{3-x}$H films prepared at different NH$_3$ to SiH$_4$ flow ratio ($R$), in the plasma. (b) Variation of $I_{220}/I_{111}$ and the grain size calculated from Debye-Scherrer formula, using the FWHM of <111> diffraction peak of XRD spectra, with $R$.](image-url)
thermodynamically preferred grains [22,23]. The nature of the variation of \(I_{(220)}/I_{(111)}\) indicates the formation of a larger amount of thermodynamically preferred crystalline grains, in the nitrogenated silicon network.

### 3.3.2 Structural Investigation by Raman Scattering

Fig. 3.2 represents first order normalized Raman spectra of the samples prepared at different \(R\). For the sake of comparison, Raman spectra of crystalline silicon (c-Si), recorded using the same setup, is also included in the same figure. The power density of the Raman laser was the same for all samples and equal to 2.0 mW/cm\(^2\), which is considered as sufficiently small for any thermal or crystallization effects to be induced on the samples. Continuous down shift of peak frequency in the Raman Spectra and a nonstop asymmetric broadening in the Raman line shape have been observed for samples prepared at different \(R\), as \(R\) increases from 0 to 0.5, attributing modification in the nature of the network structure with simultaneous reduction of the crystalline grain size. For crystalline Si (c-Si), the Raman peak is a sharp and nearly Lorentzian band centered at 520 cm\(^{-1}\) and with a full width at half

![Figure 3.2: First order normalized Raman spectra for different \(R\). Red shift of peak frequency and changes in the band shape have been indicated by arrow (→). Inset presents (a) the deconvolution of Raman spectrum into three satellite components and (b) enlarged pick view of the Raman spectra.](image-url)
maximum (FWHM) of about 3.5 cm\textsuperscript{-1} [24–26]. Raman spectrum for amorphous Si (a-Si:H) is characterized by four bands, the most intense one being the TO mode located at 480 cm\textsuperscript{-1}. Quantitative estimation of the crystalline volume fraction has been performed by the deconvolution of each Raman spectrum into three Gaussian components of which the typical features are shown in the inset (a) of Fig. 3.2. The component in the higher frequency side represents nanocrystalline part of the material and the lower frequency component arises from amorphous part, whereas the intermediate one corresponds to the ultra-nanocrystalline and/or the grain boundary component. The nano-crystalline ($X_{nc}$) and ultra-nanocrystalline ($X_{unc}$) volume fractions were estimated from the relations, $X_{nc} = I_{nc}/[I_{nc} + I_{unc} + \rho(L)I_a]$, and $X_{unc} = I_{unc}/[I_{nc} + I_{unc} + \rho(L)I_a]$, where $I_{nc}$, $I_a$ and $I_{unc}$ are the integrated intensities of the crystalline, amorphous, and ultra-nanocrystalline components, respectively, and $\rho$ is given by: $\rho(L)=0.1+exp[-(L/250)]$, which is the ratio of the integrated Raman cross-sections of the crystalline and the amorphous part and that approaches to 1 for small crystals [27]. The total crystalline volume fraction ($X_C$) has been estimated as: $X_C = X_{nc} + X_{unc}$.

In order to analyze the changes in the Raman lineshape and to calculate the average size of the crystallites, it is needed to obtain the modes allowed in the finite system, using the boundary condition that the phonon amplitude is zero at the particle boundary. In bulk crystals only $q = 0$ (zone center) optical phonon are allowed whereas, in the nanocrystals several phonon mode frequencies corresponding to the discrete allowed wave vectors contribute to the Raman intensity. This results in asymmetric broadening of the Raman lineshape. The Raman lineshape can be calculated by addition of the contribution from each of these modes (having their own natural linewidth) with suitable $q$-dependent weight or intensity factors. However, the intensity of the individual modes is not easy to calculate and hence phenomenological approach has been used to analyze the Raman lineshape. The phonon wave function cannot propagate beyond the crystal lattice. Hence, for a material containing finite size of the crystalline grains, a confinement function has to be multiplied with the continuous phonon wave function of the infinite crystal lattice, so that the propagation of the phonon wave function would be constrained within the crystal lattice. One may consider the confinement wave function as Gaussian, which has been extensively used by many researchers [24–26] as Gaussian function fits well with several boundary
value problems, from classical to quantum physics, where the function decays and has a definite value at the boundary. Therefore, the phonon wave function in a nanocrystal of size $L$ can be written as,

$$
\Psi(q_0, \mathbf{r}) = W(r, L) \Phi(q_0, \mathbf{r}) = \Theta(q_0, \mathbf{r}) \varTheta(q_0, \mathbf{r})
$$

(3.1)

where $\Phi(q_0, \mathbf{r}) = \varTheta(q_0, \mathbf{r}) e^{-i q_0 \cdot \mathbf{r}}$, wave function for a phonon of wave vector $q_0$ in an infinite crystal and $W(r, L)$ is the phonon confinement function, having Gaussian form as,

$$
W(r, L) = \exp\left(-\alpha r^2 / L^2\right)
$$

(3.2)

The value of $\alpha$ decides how rapidly the wave function decays as one approaches the boundary of the particle. Expansion of $\Theta(q_0, \mathbf{r})$ in a Fourier series introduce Fourier coefficients $c(q_0, \mathbf{q})$, which estimates the contributions of phonons away from the zone centre, can be determined from the relation, given by

$$
c(q_0, \mathbf{q}) = \frac{1}{(2\pi)^3} \int d^3r \Theta(q_0, \mathbf{r}) e^{-i \mathbf{q} \cdot \mathbf{r}}
$$

(3.3)

For the spherical nanocrystal and Gaussian confinement function with the assumption that $q_0 = 0$, which is appropriate for one phonon scattering, the Fourier coefficients are

$$
|c(0, \mathbf{q})|^2 \approx \exp\left(-q^2 L^2 / 2\alpha\right)
$$

$$
\approx \exp\left(-\pi^2\right)
$$

(3.4)

Here we have used the value of $\alpha = 2$, as same as used by Richter et al. [24] and $q = \pi / (\sqrt{\gamma})$. Surface-to-volume ratio is another important factor for the modification of Raman lineshape. It has a strong effect on the phonon frequency of crystalline like mode for nanocrystalline materials. The differences in the degree of freedom for the surface atoms and atoms inside the bulk contribute significantly in surface-to-volume ratio, which in turn describe quantitatively the relative proportions of surface and bulk phonons in a small nanocrystal, result of which is a contribution in the modification of Raman lineshape function of crystalline like mode. Mavi et al. [28] included this factor in the lineshape function of the crystalline like mode by multiplying the usual expression by $(\gamma L)$, where $L$ is the size of the nanocrystal.
Considering the partial confinement of the phonon wave function within the volume of the nanocrystal, the first order Raman spectrum can be represented as,

\[
I(\omega) \approx \frac{1}{L} \int \frac{d^3q}{[\omega - \omega(q)]^2 + (\Gamma_0 / 2)^2} \left| c(0,q) \right|^2 \\
\approx \frac{1}{L} \int \frac{d^3q \exp(-\pi^2)}{[\omega - \omega(q)]^2 + (\Gamma_0 / 2)^2}
\]

(3.5)

where \(\omega(q)\) is the phonon dispersion curve, \(\Gamma_0\) is the natural line width (inversely proportional to the intrinsic phonon lifetime), and \(L\) is the nanocrystal size. The idea of mode shifting of the zone centre phonons (ZCP) mode \((\omega_0)\) due to the localization of the phonon wave function inside a nanocrystal and the corresponding surface-to-volume correction, is being reflected from Eq. (3.5). The atoms at the surface of a nanocrystal vibrate anharmonically and the vibration of a surface atom gets affected by a number of neighboring nanocrystals. Considering sharing of atomic vibration between two neighboring nanocrystals, on the average, Mavi et al. introduced a sharing factor as \(\frac{1}{2}\) [28]. In order to estimate a better accuracy in the sharing of interaction on a surface atom by a number of adjacent nanocrystals, we consider the three dimensional distribution of the nanocrystals within the matrix as a unit of ‘Triangular Pyramid,’ where the nanocrystals are located at the vertices and the space between the particles is filled up with the matrix. The entire material grows by the repetition of the unit of Triangular Pyramid. Considering the effect of vibrational interaction on the atom at the surface of the host nanocrystal by three adjacent nanocrystals at the vertices of the unit of Triangular Pyramid, the phonon softening in the Raman line-shape leads to the phenomenological relation

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

(3.6)

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. Eq. (3.6) establishes a relation between Raman shift \((\omega_L - \omega_0)\) and size of the nanocrystal \((L)\).

The average size of the nanocrystals for different \(R\), has been estimated using the Eq. (3.6) and shown in the Table 3.1. Variation of the peak frequency and FWHM of the Raman line and crystalline volume fraction estimated there from, have also been
Table 3.1: Raman data for the nc-Si/a-SiNx:H films prepared at different NH₃ to SiH₄ flow ratio, R.

<table>
<thead>
<tr>
<th>Sample for different R = NH₃/SiH₄</th>
<th>Nanocrystalline peak position (cm⁻¹)</th>
<th>Intermediate (ultrananocrystalline) peak position (cm⁻¹)</th>
<th>Amorphous peak position (cm⁻¹)</th>
<th>FWHM of nanocrystalline component (cm⁻¹)</th>
<th>Total crystalline volume fraction (X_C)</th>
<th>Average grain size, d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>517</td>
<td>510</td>
<td>482</td>
<td>9.1</td>
<td>92.4</td>
<td>14</td>
</tr>
<tr>
<td>0.1</td>
<td>516.2</td>
<td>507.5</td>
<td>480</td>
<td>11.2</td>
<td>80.2</td>
<td>9.8</td>
</tr>
<tr>
<td>0.2</td>
<td>515.2</td>
<td>506</td>
<td>476</td>
<td>13.2</td>
<td>66.0</td>
<td>6.6</td>
</tr>
<tr>
<td>0.4</td>
<td>514.0</td>
<td>503</td>
<td>472</td>
<td>15.2</td>
<td>57.5</td>
<td>4.4</td>
</tr>
<tr>
<td>0.5</td>
<td>511.3</td>
<td>494</td>
<td>466</td>
<td>18.0</td>
<td>50.2</td>
<td>2.6</td>
</tr>
</tbody>
</table>

included. From Table 3.1, it is seen that the crystalline peak is located at around ~517 cm⁻¹ for the sample prepared at R = 0 whereas, the amorphous and intermediate peaks are observed in the vicinity of 482 and 510 cm⁻¹ respectively. The total crystalline volume fraction (X_C) for this sample has been estimated as ~92.4%, while the average size of the crystalline grain (L) as ~14 nm. Introduction of ammonia in the plasma at

Figure 3.3: Variations of (a) total crystalline volume fraction (X_C) and ultrananocrystalline/grain-boundary volume fraction (X_unc) with R, and (b) Nano-crystalline peak positions, grain size, and FWHM of the associated Raman component of the films as functions of R.
the lowest amount (0.2 sccm, defined by $R = 0.1$), decreases the network crystallinity to 80.2% whereas, average grain size reduces to 9.8 nm. Further increase of the NH$_3$ flow rate decreases the total crystalline volume fraction ($X_C$) gradually, following the curve shown in Fig. 3.3(a). However, the volume fraction ($X_{unc}$) due to ultra-nanocrystalline and/or grain boundary component, which also contributes to the total amount of crystallinity, increases monotonically with increase of NH$_3$ flow rate, the variation of which has been included in the same figure. The opposite nature of changes of $X_C$ and $X_{unc}$ with $R$ identifies a definite modification of the network wherein ultra-nanocrystalline component dominates the crystallinity within mostly amorphous nitrogenated network structure. At $R = 0.4$, crystallinity reaches to ~50% with average grain size ~2.6 nm, whereas the network structure is mostly amorphous ($X_a$ ~58%), containing ~27.5% of ultra-nanocrystalline grains ($X_{unc}$) in overall crystalline volume fraction ($X_C$) of ~42% with average grain size ~2.2 nm. The variation of the nanocrystalline peak position, peak width (FWHM) and average size measured from Raman spectra with $R$, have been shown in the Fig. 3.3(b). The average size of the nanocrystals decreases, corresponding to the continuous shift of peak position towards lower frequency side whereas, a spontaneous increase in FWHM is observed, as $R$ increases from 0 to 0.5.

### 3.3.3 Spectroscopic Ellipsometry

Fig. 3.4 represents a plot of the imaginary part of the pseudo dielectric function $<\varepsilon_2>$ with energy, extracted from the spectroscopic ellipsometry data for samples prepared at different $R$. In the non-interference range, the spectra consist of one peak around 3.4 eV ($E_1$ optical transition) and a less intense shoulder near 4.2 eV ($E_2$ optical transition). The $E_2$ optical transition is being observed in crystalline silicon and this is a strong evidence of the presence of a crystalline Si structure in the films [29,30]. It is seen from the figure that, a radical change in the shapes of the spectra has been observed as $R$ goes from 0 to 0.1 and then the spectrum changes gradually for the rest. For $R = 0$, the peaks of the $<\varepsilon_2>$ spectra are sharp and distinct. The successive broadening of two peaks of each spectrum, as $R$ goes from 0.1 onwards, has been observed and finally they merge to form a unique broad hump, representative of amorphous dominated structure. For $R = 0.1$ to 0.5 the $<\varepsilon_2>$ spectra identify a shift of the $E_2$ peak towards lower energy along with a broadening of the $E_1$ peak (3.4 eV).
These features have been attributed to the decrease of the crystallite size and the amount of crystallinity [31]. As compared to the intrinsic $<\varepsilon_2>$ response of c-Si, all these spectra represent the characteristics of crystalline silicon together with amorphous component i.e., a mixed phase material.

### 3.3.4 Estimation of Optical (Tauc) Gap

The optical gap ($E_g$) was estimated by measuring the absorbance and reflectance of the films in the UV-vis region using the following equation known as Tauc’s equation: [32]

$$\alpha h\nu = A (h\nu - E_g)^n$$  \hspace{1cm} (3.7)

where $E_g$ is the optical gap corresponding to a particular transition in the film, $\alpha$ is the absorption coefficient, $A$ is a constant, $\nu$ is the frequency of the transmitted light and the exponent $n$ characterizes the nature of band transition. Values of $n = 1/2$ and $3/2$ correspond to direct allowed and direct forbidden transitions, $n = 2$ and $3$ are related to indirect allowed and indirect forbidden transitions. The nc-Si/a-SiNx:H thin film is a mixed phase material and the value of the optical (Tauc) gap, $E_g$ may not give the exact estimation of the band gap. However, the above relation can be used to estimate...
an approximate band gap of such material. In case of mixed phase of crystalline amorphous and grain boundary, band gap should lie between amorphous and crystalline depending upon the phase fractions. Using \( n = 2 \), considering an approximation of indirect transitions, the plot of \((ahv)^{1/2}\) with \( hv \) gives the value of \( E_g \). The variation of \( E_g \) with NH\(_3\) to SiH\(_4\) flow ratio \( (R) \) is shown in Fig. 3.5. The slope of the \( E_g \) curve is maximum for \( R = 0 \) to \( R = 0.1 \) transition and then it decreases gradually. The gradual widening of optical gap, in the range 1.80–2.75 eV, has been observed as a result of increasing flow rate of NH\(_3\) in the plasma.

3.3.5 Infrared Absorption Study

The silicon–nitrogen, and silicon–hydrogen bonding configurations in the network were investigated from infrared absorption studies using FTIR spectrophotometer. The nitrogen content, \( x \) in SiN\(_x\) for this series of films was determined from the Si-N asymmetric stretching mode vibration (~840 cm\(^{-1}\)), following Hasegawa et al. [33] as

\[
x = \frac{A_\omega}{N_{Si}} \int \alpha(\omega) d\omega
\]

where, the oscillator strength, \( A_\omega = 6.7 \times 10^{18} \) cm\(^2\) and \( N_{Si} = 5 \times 10^{22} \) cm\(^{-3}\) is the atomic density of crystalline silicon. The hydrogen content (hydrogen atom bonded with Silicon), \( c \) was determined from the Si-H wagging mode vibration (~630 cm\(^{-1}\)) [34] as
CHAPTER 3  The nc-Si/a-SiNₓ:H thin films: synthesis and characterization for device applications

Figure 3.6: Variation of bonded hydrogen content, c and nitrogen content, x in SiNₓ as a function of R.

\[
c = \left[ \frac{A_\omega}{N_{Si}} \int \frac{\alpha(\omega) d\omega}{\omega} \right] \times 100\%
\]

where, \( A_\omega = 1.6 \times 10^{19} \text{ cm}^{-2} \) and \( N_{Si} = 5 \times 10^{22} \text{ cm}^{-3} \).

Variations of x and c with R have been presented in Fig. 3.6. The film prepared at \( R = 0 \) contains very low amount (\( \sim 2 \text{ at.\%} \)) of bonded hydrogen, characteristic of crystalline network. Introduction of ammonia in the plasma increases the amount of bonded hydrogen in the network and further increase of it amplifies the hydrogen content gradually. The nitrogen content also increases monotonically with the increase of ammonia flow. At \( R = 0.1 \), the network contains \( \sim 3 \text{ at.\%} \) bonded hydrogen and a little amount of nitrogen (x \( \sim 0.06 \)). Both c and x attain their highest magnitude (c \( \sim 10.7 \text{ at.\%} \) and x \( \sim 0.73 \)) at \( R=0.5 \), where the network structure is amorphous dominated, however contains maximum ultra-nanocrystalline component. For uniform comparison, thickness of all films was maintained at \( \sim 3000 \text{ Å} \).

3.3.6 Atomic Force Microscopy (AFM)

The surface morphology and roughness of the deposited films were studied using atomic force Microscope and the corresponding topographic images for the films prepared at \( R = 0 \) and 0.3 are shown with their 2D and 3D images in Fig. 3.7. The
surface of the sample at $R = 0$ is composed of different size clusters, very few isolated grains, and pits. Careful observation reveals that the space between the large clusters is filled up with different smaller clusters and grains, providing a good packing of the network without nitrogenation, at the optimized parametric condition. However, large variation in cluster size enforces higher surface roughness. On the contrary, a uniform cluster density with very small deviation in the clusters size is observed in the nitrogenated network at $R = 0.3$. The size of the clusters reduced significantly and that led to a reduced void density on the surface of nitrogenated films. The root mean square surface roughness ($\delta$), as estimated from the statistical analysis of AFM images, has been found to reduce from 25 to 3.4 nm for the films prepared at $R = 0$ and 0.3, respectively. Many of the works using glow discharge plasma-CVD report that the highest crystalline film provides the lowest surface roughness and void density while the deviation in crystallinity induces surface roughness [35–38]. However, an opposite

Figure 3.7: 2D and 3D AFM images of the films prepared at $R = 0$ and $R = 0.3$. 
Figure 3.8: TEM micrographs with low and high magnifications for the nc-Si/a-SiNₓ:H films prepared at \( R = 0, 0.2, 0.3 \) and 0.4. Corresponding histograms demonstrate the distribution of number density with size of the Si nanocrystals, in each case. The graph at the bottom demonstrates the variations of average size of the Si nanocrystals with corresponding number density and sharpness of distribution (FWHM) as a function of optical band gap, \( E_g \).
nature of variation of the surface roughness with crystallinity, observed from the present work, identifies a different growth mechanism associated with high density plasma in ICP-CVD.

### 3.3.7 Transmission Electron Microscopy (TEM)

Details of internal microstructure were investigated using high-resolution TEM. The plan-view HR-TEM micrographs of the samples corresponding to \( R = 0, 0.2, 0.3 \) and 0.4 have been displayed in Fig. 3.8. In the high magnification bright field images the Si nanocrystals embedded into the a-SiNx:H matrix are observable with prominent lattice planes with mostly \(<111>\) and \(<220>\) crystallographic orientations and few of the individual nanocrystals are demonstrated by circular marks. The matrix seems to have a crystalline volume fraction \(<50\%\) which is different from that estimated from Raman studies and that is because of the very low thickness of the TEM samples, \(\sim 300–400 \text{ Å}\) which is insufficient for attaining saturation in crystallinity. The nanocrystals are randomly distribution in the amorphous matrix and are separated from each other. A Gaussian like distribution of nanocrystals in each micrograph is presented by the corresponding histograms. The average size and number density of the nanocrystals have been identified from the corresponding peak of the distributions. It is demonstrated by the plot in Fig. 3.8 that the average size of the Si nanocrystals reduced monotonically from 12 to 2.6 nm with corresponding increase in the number density from \(~3.5\times10^{11}\) to \(1.5\times10^{12} \text{ cm}^{-1}\) with simultaneous narrowing in the sharpness of distribution, as \(\text{N/Si ratio in the network increased by associated increase in } R \leq 0.4\), before the network turned to mostly amorphous dominated at \( R = 0.5\).

Fig. 3.9(a) shows the HRTEM image consisting of a large number of well separated small nanocrystals of diameter \(\sim 2.6 \text{ nm}\), spreading over the amorphous SiNx:H, prepared at \( R = 0.4\), containing \(~50.2\%\) crystallinity as measured from Raman spectra. The bright diffuse rings in the selected area electron diffraction (SAED) pattern (Fig. 3.9(b)) indicate the existence of tiny crystalline grains with two prominent orientations, \(<111>\) and \(<220>\), having interplaner spacing 0.312 nm, and 0.198 nm respectively; while the less prominent ring represents \(<311>\) orientation with interplaner spacing 0.165 nm. The magnified images of both the \(<111>\) and \(<220>\) oriented nanocrystals are shown separately in Fig. 3.9(c) and (d). Fig. 3.10 represents
Figure 3.9: (a) HR-TEM image of the nc-Si/a-SiNx:H films at $R = 0.4$ (b) corresponds to its SAED pattern, (c) and (d) represent high magnification images of (111) and (220) oriented planes, respectively.

Figure 3.10: HR-TEM image of a typical silicon nanocrystal, showing the (111) lattice plane orientation and an average nanocrystallite size of $\sim 12$ nm for the sample prepared at $R = 0$. 
the high magnification image of a <111> oriented single nanocrystal of the film prepared at \( R = 0 \). This material contains nanocrystallites of average size ~12 nm with highest amount of crystallinity ~92%. The average grain size of the nanocrystals at \( R = 0.2 \) has been estimated as ~6.5 nm, corresponding to ~66% of its Raman crystallinity.

### 3.3.8 Photoluminescence

The photoluminescence (PL) spectrum for the sample prepared at \( R = 0.4 \) and 0.5 with uniform excitation of 325 nm by a He-Cd laser is shown in Fig. 3.11. Both the samples show bright blue PL having distinct double-peak spectrum (a) and (b) and two shoulders (c) and (d). Each spectrum broadens asymmetrically in the longer

**Figure 3.11:** A broad blue PL band having four satellite components, showing double peaks at ~413 nm and ~438 nm with two shoulders at ~467 nm and ~498 nm, for the sample prepared at (a) \( R = 0.4 \) and (b) \( R = 0.5 \).
wavelength side. In order to interpret the asymmetrically broaden PL spectrum, it is needed to fit the spectrum into a number of peaks. We have identified that in the fitting procedure Gaussian peaks are best fitted, as shown by four satellite components. The sample prepared at $R = 0.4$ contains peaks at 413 nm (3 eV), 438 nm (2.83 eV), 467 nm (2.65 eV), and 498 nm (2.49 eV) and the positions of the four corresponding peaks for $R = 0.5$ are at 413 nm (3 eV), 438 nm (2.83 eV), 467 nm (2.65 eV), and 496 nm (2.5 eV), respectively. Careful observation reveals that concerning the double-peak spectrum, the intensities of the component ‘a’ and ‘b’ are nearly equal at $R = 0.4$ whereas, the relative intensity of the component ‘b’ increases significantly at $R = 0.5$. While within the asymmetric shoulder part of the spectrum, the relative intensity of the component ‘d’ increases to that of ‘c’ as $R$ varies from 0.4 to 0.5.

### 3.3 Discussion

The plasma-assisted growth process of hydrogenated nc-Si within amorphous silicon-nitride matrix involves three main sets of elementary reactions, namely primary decomposition of the precursor gases via electron impact reactions, secondary gas-phase reactions among the radicals and the source gas molecules, and finally, surface reactions on the substrate [39]. The atomic hydrogen flux and the energy of ion species impinging on the growing surface play a crucial role in the formation process of nc-Si/a-SiN$_x$:H [40–42]. In contrast to the conventional capacitively coupled system, Inductively Coupled reactor (ICP) provides higher density of the plasma, which is often advantageous for the growth of less defective and more crystalline films that are important requirements in device application [43]. From Fig. 3.3(a), it is seen that the total crystallinity, estimated from Raman spectra, varies from ~92.4% to ~42%, as $R$ goes from 0 to 0.5. Such high magnitude of crystallinity is the unique feature of high-density inductively coupled plasma, in which the high dissociation of SiH$_4$ and NH$_3$, even without of H$_2$ dilution, provides very high surface coverage by large amount of atomic hydrogen flux. This high surface coverage by atomic hydrogen increase surface diffusion length of the radicals through lower magnitude of surface diffusion activation energy [44]. Large surface diffusion length makes possible of having higher amount crystallinity in the network compared to the material synthesized by capacitively coupled plasma.
A decrease of Raman crystallinity results from the increasing nitrogen incorporation in the network at higher NH$_3$-dilution in the plasma, however, the ultra-nanocrystalline component enhances in intensity and the average grain size efficiently reduces. The reduction in the average grain size has been monitored by continuous red shift of peak frequency of the Raman line, as NH$_3$ flow rate is increased. The shift is usually attributed to the phonon confinement within the Si nanocrystals. The fitting of the Raman spectrum into three Gaussian peaks, shown in the inset of Fig. 3.2, assisted in the quantitative estimation of the crystalline volume fraction. Fitting by the Gaussian peaks is well acceptable in describing the Raman analysis of nc-Si. The usual Lorentzian shape of the crystalline component in the higher frequency side should be replaced by a Gaussian curve for small crystallites, having size less than ~13 nm [27]. It is noted that the frequency corresponding to the component representing the TO mode of amorphous silicon is downshifted due to the presence of Si–N bonds in the amorphous matrix [45].

In order to make a comparative study on the variation of grain sizes, those calculated using different models of first order Raman spectra, estimated using <111> diffraction peak of XRD spectra, and the average crystallite size measured directly from the HR-TEM have been plotted in Fig. 3.12. In Correlation Length Model (CLM) [25,26] and Bond Polarizability Model (BPM), the size of the Si nanocrystals was calculated using the relation established by Zi et al. [46]:

\[
\Delta \omega (L) = -A \left( \frac{a}{L} \right)^{\gamma}
\]  

(3.10)

where $\Delta \omega$ is the Raman shift in a nanocrystal with diameter $L$, $a$ is the network constant of Si ($a = 0.543$ nm), $A$ and $\gamma$ are fit parameters that describe the phonon confinement in nanometric grains. Depending on the different form of phonon weighting function and corresponding individual boundary condition, the values of fit parameters are different in different models. The parameters $A$ and $\gamma$ are the following: (i) for the CL model $A = 97.462$ cm$^{-1}$ and $\gamma = 1.39$; (ii) for the BP model $A = 47.41$ cm$^{-1}$ and $\gamma = 1.44$. These two models represent variation of grain size in narrow range. Size of the nanocrystals calculated from the width of <111> peak of the XRD spectra, using Debye-Scherrer formula, closely resembles to that estimated using the phenomenological Eq. (3.6) in the Raman spectra. An overestimation of size
Figure 3.12: Variation of the grain size of Si nanocrystals calculated using different models of the first order Raman spectra, including the present work. Size estimated from the XRD and HR-TEM data have been included in the same figure for comparison.

appears following Mavi et al. using the sharing factor as $\frac{1}{2}$ [28]. Instead, our presently modified sharing factor, $1/3$, involving surface-to-volume interaction in Eq. (3.6), provides a fairly acceptable solution to the estimation of grain size from Raman data, showing close proximity with that obtained from X-ray diffraction and HR-TEM observation. The ellipsometry result is also consistent with the systematic decrease of network crystallinity and reduction in grain size as a function of increasing NH$_3$ flow rate in the plasma, obtained from Raman and XRD data.

The number of the thermodynamically preferred crystalline grains in the material, exhibiting relative dominance of $<220>$ crystallographic orientation, increases with the increase of $R$. The thermodynamically preferred grains are important for device application of the material. It is reported in the literature that the performance of solar cells depends strongly on the XRD $I_{(220)}/I_{(111)}$ intensity ratio [21,47–49]. Best values of open-circuit voltage ($V_{OC}$) in solar cells identifies low recombination losses in (220) textures. Under particular plasma-CVD conditions near the amorphous to nanocrystalline Si transition region, a higher (220) peak intensity is reported compared to that for highly crystalline Si [47,48]. In some cases it has been observed that the $I_{(220)}/I_{(111)}$ peak height ratio is greater than 1. That stems from the
larger volume fraction of <220> oriented grains compared to <111> oriented grains in the nc-Si thin film [47–49], more specifically, the (220) grains are longitudinally larger in size [47]. The charge carriers, whose conduction path is perpendicular to the substrate in the nc-Si solar cells, witness fewer grain boundaries under <220> oriented grains than it do for <111> oriented grains. Additionally, the predominance of the amorphous volume fraction helps to efficiently passivate the grain surface. The combination of these two phenomena serves to reduce bulk recombination and/or field losses in the thin film solar cell and thereby increases the \( V_{OC} \) and Fill Factor (FF) of the nc-Si solar cells, respectively.

The microstructure of the present nc-Si/a-SiNx:H films is composed of silicon nanocrystals, closely packed together to form nano sized conglomerates, surrounded by an amorphous silicon-nitride matrix. Here, the volume fraction of these crystalline conglomerates and amorphous tissue vary based on the NH\(_3\)-dilution, \( R \). It has been observed that for highly crystalline deposition conditions, not only the conglomerate volume fraction in the bulk increases steeply, but also the density of grain boundaries, voids, and cracks in the resultant thin film increases as well. This leads to carrier losses and leaves the resultant material prone to post fabrication impurity contamination from the ambient [50]. Conversely, near the transition region, it has been reported that the nanocrystals, instead of being closely packed into conglomerates, are dispersed in the amorphous matrix. This specific microstructural configuration is of device research interest, since the prevalence of the amorphous tissue serves to passivate the dangling bonds on the nanocrystal surface. Furthermore, under certain conditions, high density of elongated nanocrystals can be observed near the transition region, as well [21]. Combined effects yield larger \( V_{OC} \) and FF in the finished solar cell device. Toyoshima et al., experimenting on the nature of grain orientation in nc-Si:H, concluded two primary factors, substrate temperature and hydrogen dilution ratio, that control the predominance of <220> oriented crystals [51]. A rise in the substrate temperature favors <220> orientation. This is because, at higher substrate temperatures, the growth rate of (220) grains are far larger than (111) grains [51]. In another way, increase in the hydrogen dilution ratio in the plasma increases the volume fraction of (111) grains compared to (220) grains. During the nc-Si:H growth, a substantial preference of (111) nucleate density over (220) is observed regardless of the substrate temperature (\( \leq 300 \) °C) [48]. The specific reason behind this preference
is not yet understood. Kitagawa et al. reported that the intensity ratio of (220) to (111), $I_{(220)}/I_{(111)}$, increase with thickness [52]. Among the above factors facilitating the growth of <220> crystallographic orientation in the Si network, higher substrate temperature reduces the device feasibility on inexpensive soft substrates and higher thickness may be inappropriate for certain component layers of the device. In the present work while depositing the nc-Si/a-SiN$_x$:H thin films, the only variable which controls the growth of (220) grains, is the NH$_3$ dilution, keeping all the above factors namely the substrate temperature and thickness remaining unchanged. The increase of the XRD $I_{(220)}/I_{(111)}$ intensity ratio with NH$_3$ dilution by means of incorporation of a foreign atom, nitrogen in the network, is the novelty of this work, while it simultaneously provides a desired nitrogenated dielectric matrix for device fabrication. The nc-Si/a-SiN$_x$:H thin films with increasing (220) grains, described in the present work might be important for enhancement of the open circuit voltage, and reduction of the photo-carrier losses in solar cells. Importantly, the increase of the XRD $I_{(220)}/I_{(111)}$ ratio can be correlated to the increasing ultra-nanocrystalline and/or grain boundary component of the Raman spectra, and the simultaneous miniaturization of the nanocrystal size, facilitating quantum confinement effects [17].

The band gap (Tauc gap, $E_g$) engineering (1.80–2.75 eV) of the nc-Si/a-SiN$_x$:H thin films can be easily realized by controlling the nanocrystal size, incorporated nitrogen and the bonded hydrogen. In the present context, band gap widening occurs unidirectionally due to lowering of nanocrystal size due to quantum confinement [53,54] and increase of both nitrogen and hydrogen content in the material, while increasing NH$_3$ dilution to the SiH$_4$ plasma. In tandem structure $p$–$i$–$n$ solar cells different cells with varying individual $i$-layer band gaps are stacked together, where each cell absorbs a separate range of photon energies from the incident solar spectrum. Higher energy photons are absorbed in the higher-band-gap cells and lower-energy photons in the lower-band-gap cells, reducing the overall heat loss due to carrier relaxation via phonon emission [6,8]. Possible band gap modification of the nc-Si/a-SiN$_x$:H may lead to promising use of the material in tandem cell configuration. Properly designed nanostructures and nanostructure-arrays do not require additional light trapping layers as they naturally allow the light to enter and be trapped within the structure. Due to quantum size effect, three-dimensional quantum confined silicon dots could yield high broadband absorption through proper band-gap [6] and band-structure
engineering. In addition, SiN\textsubscript{x} matrix being good antireflector would help to enhance the efficiency in light absorption.

It is difficult to investigate the definite origin of a luminescence peak for silicon like indirect band gap material. However, it has been reported [9,19,20] that nc-Si responds positively in photoluminescence, with some specific features at the onset of nanocrystallinity [56]. The matrix silicon-nitride itself has several luminescence bands, originated from nitrogen and silicon related defect states [57]. The defect energy levels, such as $=Si^0$, Si donor energy level; $=Si^-$, Si acceptor energy level; $=N^-$, $=N$energy level as the hole traps; $=Si-Si=\equiv$, the Si-Si energy level, etc., exist in the gap of, the a-SiN\textsubscript{x} material. Oxide related defects also play vital role in visible luminescence from silicon nanocrystal, because oxygen is an inherent residual incorporation in silicon based micro- and nano-structured films [58]. There are large number of dangling bonds existing in films, especially at the interface regions between Si nanocrystals and the SiN\textsubscript{x} matrix. The existence of Si–H and N–H bonds introduced by plasma dissociation of H\textsubscript{2} and NH\textsubscript{3} passivate the nonradiative defects in films and lead to the improved PL of silicon nanocrystals embedded in the silicon nitride matrix.

In this respect, the passivation of these Si- and N-related dangling bonds is an essential requirement for increasing the radiative yield without affecting the emission mechanism. As the material contains small Si nanocrystals of average size ~2.2 nm, the nonradiative defect centers are much lesser in number compared to larger size nanocrystal because of having smaller surface area.

In explaining the origin of the two peaks at 413 nm (3 eV) and 438 nm (2.83 eV), we recall the argument made by Ivashchenko et al. [59] where both the valence and conduction band tails lie in the band gap region for small silicon nanocrystals. Tiny size of the nanocrystallites and the associated lattice distortion cause a change in the nature of the band structure from indirect to direct [19]. Based upon these discussions, the emission peak at 413 nm (~3 eV) is considered as the band-to-band recombination in the small silicon nanocrystals having size <3 nm and the 438 nm (~2.83eV) emission arises during the recombination between band-to-states, while the states appear from Si ultra-nanocrystals and/or grain boundary. In case of the present experiment, the increasing intensity of the 438 nm (~2.83 eV) emission band (Fig. 3.11), during increase in NH\textsubscript{3}-dilution, $R$ from 0.4 to 0.5, could accordingly be associated to the increasing intensity of the Si ultra-nanocrystalline and/or grain
boundary component (Fig. 3.3), while the overall network approaches towards relatively amorphous structure. The 467 nm (2.65 eV) PL peak could be attributed either to the electronic transitions of $\equiv$Si$^-$ $\rightarrow$ N$^-$ defect states [60] or neutral oxygen vacancy in the network (i.e., the $\equiv$Si$-$Si$\equiv$ center) [61–63]. The source of oxygen in the material is due to oxygen containing residuals (oxygen, water vapors, carbon oxides) adsorbed at the chamber wall. The peak at 498 nm (2.49 eV) may be originated from the radiative Si dangling bond ($K^0$) center [64] located in the middle of silicon nitride band gap. The relative increase of the 498 nm (2.49 eV) component to 467 nm (2.65 eV) component during increase in $R$ from 0.4 to 0.5 could thus be correlated to increasing NH$_3$-dilution and the subsequent weaken effect of the oxygen contaminant.

### 3.4 Conclusions

Silicon nanocrystals embedded in amorphous silicon-nitride matrix (nc-Si/a-Si$_{N_x}$:H) have been prepared using 13.56 MHz RF planer ICP-CVD, by changing the flow ratio $R = \text{NH}_3$/SiH$_4$ from 0 to 0.5, within H$_2$-diluted plasma. With the advent of high atomic H density in inductively coupled plasma having very high overall crystallinity ($X_C$) $\sim$92.4% is obtained at $R = 0$ and that reduces systematically to $\sim$42% at $R = 0.5$, while the ultra-nanocrystalline component ($X_{unc}$) increases monotonically with increase of NH$_3$ flow rate. Thus a definite modification of the network has been identified whereby ultrafine nanocrystalline component dominates the crystallinity within mostly amorphous nitrogenated network structure and a simultaneous reduction in grain size from 14 to 2.2 nm with increasing number density $\sim$10$^{11}$–10$^{12}$ cm$^{-2}$ has been monitored for $R$ varying from 0 to 0.5. A continuous red shift of the peak frequency and the broadening of first order Raman band identify a strong phonon confinement effects. Modifications to the sharing factor involving surface-to-volume interaction, led to a phenomenological relation that provides a fairly acceptable solution to the estimation of grain size from Raman spectra, showing close proximity with that obtained from X-ray diffraction and HR-TEM data. The size of the clusters reduced significantly with increasing $R$, as observed from AFM images, and that led to a reduced void density on the surface of nitrogenated films. The root mean square surface roughness ($\delta$), as estimated from the statistical analysis of AFM images, has
been found to reduce from 25 to 3.4 nm for the films prepared at $R = 0$ and 0.3, respectively.

Gradual increase in relative intensity of the (220) peak, $I_{(220)}/I_{(111)}$, in XRD pattern identified thermodynamically preferred growth of silicon nanocrystals, at <220> crystallographic orientation, when embedded within amorphous dominated nitrogenated network at increasing $R$, and that raise technological promise in photovoltaic applications. Increasing bonded hydrogen and nitrogen content and enhanced ultra-nanocrystalline component in nc-Si/a-SiN$_x$:H thin films facilitate widening in band gap (Tauc gap, 1.80–2.75 eV) while possible band gap engineering could yield high broadband absorption, useful in the fabrication of third-generation all-silicon tandem cells.

The nc-Si/a-SiN$_x$:H films exhibit strong blue light emission that consist of two peaks at 413 nm and 438 nm, and two shoulder around 467 nm and 498 nm. The emission peak at 413 nm is considered to originate from the band-to-band recombination in the small silicon nanocrystals having size < 3 nm and the 438 nm emission arises during the recombination between band-to-states, while the states could appear from Si ultra-nanocrystals and/or grain boundary.

Among the factors previously reported to facilitate the growth of (220) crystallographic orientation in the Si network, higher substrate temperature reduces the device feasibility on inexpensive soft substrates and higher thickness may restrict its use in certain component layers of the device. The novelty of the present work is that, the development of Si nanocrystals of continuously reducing size down to 2.2 nm and increasing volume fraction of the ultra-nanocrystalline component up to 27.5%, with simultaneous thermodynamically favorable <220> preferential crystallographic orientation ($I_{(220)}/I_{(111)} \sim 1$) has been possible at low substrate temperature (300 °C), and at low thickness. The growth has been controlled simply by incorporating N within Si network, which thereby provides the nitrogenated dielectric matrix that embraces the Si-ncs and simultaneously contributes high dielectric constant and low tunneling barrier, which in turn facilitate applications in devices. Band gap widening and enhanced blue emission demonstrates quantum size effects and ascertains further device feasibilities e.g., solar cells and light emitting devices.
CHAPTER 3
The nc-Si/a-SiNₓ:H thin films: synthesis and characterization for device applications

Bibliography

CHAPTER 3  The nc-Si/a-SiNx:H thin films: synthesis and characterization for device applications
