List of Figures

Figure 1.1: (a) Face-Centre diamond lattice structure of the unit cell of crystalline silicon (b) Schematic presentation of the order structure of crystalline silicon lattice (c) Realistic band structure of the c-Si………………………………………………………………………… 6

Figure 1.2: Lattice of hydrogenated amorphous silicon…………………………………… 8

Figure 1.3: 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)……… 9

Figure 1.4: E-k diagrams of electron transition from the conduction band to empty (hole) states in the valence band for (a) direct band–gap materials such as GaAs, a-Si (quasi-direct) and (b) indirect band-gap materials such as c-Si………10

Figure 1.5: Schematic illustration of the structure of μc-Si:H…………………… 11

Figure 1.6: Schematic diagram illustrating the microstructural characteristics of μc-Si:H obtained for growth on foreign substrates. From the left to the right, the film composition changes from highly crystalline to predominantly amorphous (From [42])………………………………………………………………………………… 12

Figure 1.7: Absorption coefficient $\alpha$ vs. energy for a-Si:H, μc-Si:H and crystalline silicon (c-Si) [57]………………………………………………………………………………….. 13

Figure 1.8: Schematic energy band diagram of silicon showing electron excitation and absorption in silicon. Blue arrows indicate indirect absorption. Red arrows indicate phonon assisted indirect radiative recombination. Purple arrow shows non-radiative recombination and green arrows show Auger recombination. Orange arrows indicate free-carrier absorption…………………………………… 16

Figure 1.9: Schematic of the low-dimensional structure and the density of states (DOS) as a function of the energy for a particle constrained to move in the bulk (3D), in a Q-well (2D), in Q-wire (1D) and in a Q-dot (0D)……………… 18

Figure 1.10: Si quantum dots have diverse applications in microelectronics, photonics and photovoltaics………………………………………………………………………………… 21

Figure 1.11: (a) Bulk band alignments between crystalline silicon and SiO$_2$, Si$_3$N$_4$ and SiC. (b) The band gap increases for quantum confined silicon dots of 3 nm diameter to 1.73 eV [128]. To ensure tunneling between silicon dots embedded in SiO$_2$, the distance between dots should be less than 2 nm……………… 23

Figure 2.1: Scheme of an RF discharge in a parallel-plate reactor with capacitive coupling of the RF generator; together with the spatial distributions of potential voltage $V$ (plasma potential $V_p$, bias voltage $V_b$, and anode voltage $V_a$)………………………………………………………………………………… 38
Figure 2.2: ICP-CVD facility at Energy Research Unit, Indian Association for the Cultivation of Science

Figure 2.3: Schematic diagram of the main deposition chamber in ICP-CVD unit.

Figure 2.4: Schematic diagram for thickness measurement by stylus profilometer.

Figure 2.5: Basic XRD diagram.

Figure 2.6: Some of the possible molecular vibrations for two identical atoms bonded to a third dissimilar atom [37].

Figure 2.7: Schematic diagram of the FTIR instrument.

Figure 2.8: Schematic of XPS system.

Figure 2.9: Micro-Raman spectrometer composed of an Ar laser source, a microscope, a notch filter, a grating and a CCD camera.

Figure 2.10: Geometry of basic ellipsometry principal.

Figure 2.11: Schematic of an ellipsometer instrument.

Figure 2.12: The basic structure of a TEM.

Figure 2.13: Positions of different lenses and images formed along with the cross-sectional view of an electromagnetic lens.

Figure 2.14: Mounted XTEM sample on TEM grid, ready for ion milling.

Figure 2.15: Schematic diagram of FE-SEM indicating different parts.

Figure 2.16: Schematic diagram of a tapping mode AFM.

Figure 2.17: Schematic diagram of photon absorption and emission for direct and indirect band gap semiconductor.

Figure 2.18: Schematic of the spectroscopic photoluminescence set-up.

Figure 2.19: The band diagram of silicon.

Figure 2.20: Schematic of Van der Pauw Analysis of Thin Films.

Figure 3.1: (a) X-ray diffraction spectra of nc-Si/a-SiNx:H films prepared at different NH3 to SiH4 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.

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.

**Figure 3.3:** Variations of (a) total crystalline volume fraction ($X_C$) and ultrananocrystalline/grain-boundary volume fraction ($X_{unc}$) with $R$, and (b) Nanocrystalline peak positions, grain size, and FWHM of the associated Raman component of the films as functions of $R$.

**Figure 3.4:** Imaginary part of the pseudo-dielectric function ($\varepsilon_2$) for Different $R$, measured from spectroscopic ellipsometry experiment.

**Figure 3.5:** Variation of optical (Tauc) gap as a function of $R$.

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

**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, $E_g$.

**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 ~12 nm for the sample prepared at $R = 0$.

**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) $R = 0.5$.

**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.

**Figure 4.1:** Variation of the optical (Tauc) gap, $E_g$ as a function of NH$_3$ to SiH$_4$ flow ratio ($R$), in the plasma.

**Figure 4.2:** Variations in the room temperature dark conductivity ($\sigma_d$), photo conductivity ($\sigma_{ph}$) and the corresponding photosensitivity ($S$) as a function of increasing optical (Tauc) gap, $E_g$ for the nc-Si/a-SiNx:H films prepared at increasing $R$. 
Figure 4.3: Arrhenius plot of the dark conductivity ($\sigma_d$) of the nc-Si/a-SiNx:H films prepared at different $R$. Inset demonstrates the high temperature section of the same, demonstrating the thermally activated conduction above room temperature. ................................................................. 115

Figure 4.4: Variation of the high temperature activation energy ($E_a$) with optical (Tauc) gap, $E_g$. Inset demonstrates the pre-exponential factor ($\sigma_0$) of dark conductivity as function of activation energy $E_a$. The solid line is a linear regression fit to the data ................................................................. 116

Figure 4.5: The reduced activation energy, $w(T)$, plotted against $T$ on a log-log scale for $R = 0.3$, identifying three different temperature regimes with individual slopes, in a sawtooth-like profile and recognizing three different conduction phenomena to be in effect. ................................................................. 117

Figure 4.6: (a) Plot of $\sigma_d$ vs $T$ in log-log scale, demonstrating a power-law temperature dependence of conductivity ($\sigma \propto T^{-y}$) due to multi-phonon hopping (MPH) below room temperature, with systematically enhanced $y$ for increasing $R$; and (b) variation of $\ln(\sigma_d)$ with $T^{-1/4}$ identifying Mott-VRH to be in effect, for samples with $0.3 \leq R \leq 0.5$, below certain temperature that increases with $R$. … 118

Figure 4.7: Variation of room temperature mobility ($\mu_d$) and carrier concentration ($n_e$), estimated from Hall-effect measurement, with increasing optical (Tauc) gap, $E_g$ ................................................................. 119

Figure 4.8: 3D representation of the typical XRD pattern for the nc-Si/a-SiNx:H film having wide optical gap, $E_g = 2.59$ eV, corresponding to $R = 0.3$. Inset demonstrates the variation of $I_{(220)}/I_{(111)}$ with $E_g$ ......................... 121

Figure 4.9: 3D representation of the typical first order Raman spectrum, deconvoluted into three satellite components, for the nc-Si/a-SiNx:H film having $E_g = 2.59$ eV, corresponding to $R = 0.3$. Inset demonstrates the variation of total crystalline volume fraction ($X_C$) and its ultra nanocrystalline component ($X_{unc}$) with increasing $E_g$ ......................... 122

Figure 4.10: FE-SEM images of the films prepared at $R = 0$ and $R = 0.4$ ............... 122

Figure 4.11: FE-SEM image demonstrating the columnar growth morphology of the nc-Si/a-SiNx:H network prepared at $R = 0.3$ ................................................................. 123

Figure 4.12: Comparison on the nature of variation of the optical (Tauc) gap with nanocrystallite size, estimated from XRD and Raman spectra ......................... 126

Figure 4.13: Nature of variation of the room temperature dark conductivity ($\sigma_d$) of the nc-Si/a-SiNx:H films with changes in overall crystallinity ($X_C$). Inset demonstrates the improvement of photosensitivity ($S$) with the dominance of ultra-nanocrystalline component ($X_{unc}$) present in the network ......................... 128

Figure 4.14: Variations of (a) the optimum hopping distance, $r_h$, and (b) the hopping activation energy, $W_h$, with temperature, demonstrating both having
higher magnitude for higher $E_g$, however, admitting different nature of temperature dependence………………………………………………………… 134

Figure 4.15: A comparative analysis, correlating room temperature dark conductivity and optical band gap, among various works reported on the development of silicon and silicon related dielectric films deposited by different CVD processes………………………………………………………… 136

Figure 5.1: Room temperature photoluminescence (PL) spectra of films, having nc-Si QDs embedded in a-SiN$_x$:H matrix, prepared at different substrate temperatures varying from 400 to 150 °C with an interval of 50 °C……146

Figure 5.2: Variations of (a) photoluminescence (PL) peak energy and (b) integrated PL intensity as well as FWHM, corresponding to different substrate temperature, $T$……………………………………………………………………… 147

Figure 5.3: Variation of optical (Tauc) gap, $E_g$ as a function of substrate temperature, $T$……………………………………………………………………… 148

Figure 5.4: HR-TEM image of the nc-Si/a-SiN$_x$:H films prepared at (a) $T = 350$ °C and (c) $T = 250$ °C, while, (b) and (d) represent the corresponding histograms demonstrating the variations of the number density, size and the FWHM of the distribution of the nc-Si QDs……………………………………………………………………… 149

Figure 5.5: First order normalized Raman spectra of nc-Si/a-SiN$_x$:H films prepared at different $T$. Inset represents the enlarged view of the peak of Raman spectra……………………………………………………………………… 150

Figure 5.6: (a) Variations of the size of nc-Si QDs estimated from Raman peak shift as well as measured from HRTEM image, with substrate temperature. (b) Variations of the crystalline ($X_C$) and ultra-nanocrystalline volume fraction ($X_{unc}$) with $T$……………………………………………………………………… 151

Figure 5.7: Schematic of quasi-direct recombination process in case of nc-Si QDs…………………………………………………………………………………… 153

Figure 5.8: Deconvolution of PL spectra into possible satellite components arising out of various defect contributions and quasi-direct band-to-band recombination due to quantum confinement effect……………………………………………………………………… 154

Figure 5.9: The variation of peak energy of the typical photoluminescence spectrum obtained experimentally and the specific component of PL identified as a contribution from band-to-band recombination in nc-Si QDs, originated due to quantum confinement effect plotted separately as a function of estimated size of the quantum dots……………………………………………………………………… 155

Figure 6.1: X-ray diffraction spectra of nc-Si/a-SiN$_x$:H QDs thin films prepared at different growth temperature, $T_S$, varying from 400 to 100 °C. Inset shows the variation of $Z_{(220)}$ [$= I_{(220)}/I_{(111)}$] and $Z_{(311)}$ [$= I_{(311)}/I_{(111)}$], with $T_S$……………… 165
Figure 6.2: First order Raman spectra for different \( Z_{(220)} \). Red shift of the peak frequency has been directed by arrow. Inset presents the variations of total crystalline volume fraction \( (X_C) \) and ultra-nanocrystalline volume fraction \( (X_{unc}) \) with \( Z_{(220)} \). ......................................................... 167

Figure 6.3: (a)-(d) are the HAADF STEM images of the samples prepared at growth temperature, \( T_S = 400, 250, 200 \) and \( 150 \) °C. Insets (b1) & (b2) are the elemental maps obtained by integrating the Si K and N K EDX peak intensities, respectively. For sample prepared at \( T_S = 250 \) °C. (e),(e1) and (f),(f1) are the HR-TEM micrographs with low and high magnifications for the nc-Si/a-SiNx:H QDs films prepared at \( T_S = 400 \) and 200 °C, respectively. Corresponding histograms demonstrate the distribution of number density with size of the Si nanocrystals, while the selected area diffraction pattern demonstrates the changes in the degree of crystallinity in each case........................................... 169

Figure 6.4: Comparison on the nature of variation in the size of Si-ncs estimated from various spectroscopic and microscopic studies (XRD, Raman spectra and HR-TEM) with growth temperature, \( T_S \)................................................................. 170

Figure 6.5: (a) FTIR spectra for different crystalline volume fraction \( (X_C) \) of the sample deposited at growth temperature, \( T_S \) from 400 to 100 °C with an interval 50 °C, where the characteristic features of silicon nitride, notably the Si–N symmetric and asymmetric stretching modes, the Si–H stretching and wagging modes and the N–H wagging/rocking and stretching modes, have been exhibited. Inset presents the magnified view of the variation of N-H Wagging/Rocking mode. (b) Presents the intensity variation of Si-N asymmetric stretching absorption band. Inset presents the variation of peak wavenumber of Si-N asymmetric stretching absorption band with \( T_S \). (c) Presents the variation of bonded nitrogen content, \( x \) in SiNx and hydrogen content \( C_H \) (in at.%), with \( T_S \). (d) Presents the intensity variation of Si-H stretching absorption band.............................................. 172

Figure 6.6: (a) The relative intensity, \( (I_{2100}/I_{2200}) \), variation of two components in Si-H stretching absorption band as a function of nitrogen content, \( x \). Inset presents the typical deconvolution of Si-H stretching absorption band for sample at \( T = 100 \) °C. (b) The variation of peak wave number of 2100 and 2200 components in of Si-H stretching absorption band as a function of nitrogen content, \( x \) in SiNx................................................................. 175

Figure 6.7: Variation of optical gap, \( E_g \), of nc-Si/a-SiNx:H QDs thin films as a function of nitrogen content, \( x \) in SiNx, estimated by using Tauc’s [42] and Cody’s [43] method. Inset shows the plot of optical absorption coefficient \( (a) \) versus photon energy \( (h\nu) \) for films deposited at \( T_S = 400 \) and 200°C............. 177

Figure 6.8: (a) Variations in the room temperature dark conductivity \( (\sigma_d) \), photo conductivity \( (\sigma_{ph}) \) and the corresponding photosensitivity \( (S_{ph}) \) as a function of nitrogen content, \( x \), for the nc-Si/a-SiNx:H films prepared at decreasing \( T_S \). (b) Variations of estimated electron mobility \( (\mu_e) \) and carrier concentration \( (n_e) \) of the samples prepared at \( T_S = 400, 300, 200, \) and 100 °C, grown on crystalline silicon (c-Si) substrate, with increasing nitrogen content, \( x \), in SiNx................................................................. 179
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.

Figure 7.2: Variation of optical (Tauc) gap, E₉, for nc-Si/a-SiNₓ:H QDs thin films as a function of deposition pressure, p.

Figure 7.3: (a) Low magnification HR-TEM micrograph of the nc-Si/a-SiNₓ: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.

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 μm (i.e. area is 4μm x 4μm).

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.

Figure 7.6: (a) Variations of the crystalline (Xₖ) 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.

Figure 7.7: (a) Typical FTIR spectrum of nc-Si/a-SiNₓ: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 SiNₓ and hydrogen content Cₛ (in at.%), with p, and (d) Absorption co-efficient spectrum of Si-H stretching band for films with different p.

Figure 7.8: Variation of electrical conductivity, σ, of nc-Si/a-SiNₓ:H QDs thin films as a function of deposition pressure, p.

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.

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.

Figure 8.1: Variation of the deposition rate Rd as a function of deposition
pressure, \( p \)………………………………………………………………………….. 211

**Figure 8.2:** First order Raman spectra at different \( p \). Inset presents enlarged pick view of the Raman spectra………………………………………………………………………………………………………………………….. 212

**Figure 8.3:** (a) Variations of the total crystalline volume fraction (\( X_C \)% ) and ultra-nanocrystalline volume fraction (\( X_{unc} \)% ) with deposition pressure, \( p \). (b) Variations of the size of nc-Si QDs estimated from the red shift of the first order Raman spectra with \( p \)…………………………………………………………………………………………………………………….. 213

**Figure 8.4:** X-ray diffraction spectra of nc-Si/a-SiN\(_{x}\):H QDs thin films prepared at different pressure, \( p \), varying from 10 to 60 mTorr. Inset shows the variation of \( I_{(220)}/I_{(111)} \), with \( p \)…………………………………………………………………………………………………………………….. 214

**Figure 8.5:** (a),(b) and (c),(d) are the HR-TEM micrographs with low and high magnifications for the nc-Si/a-SiN\(_{x}\):H QDs films prepared at \( p =30 \) and 10 mTorr, respectively. Corresponding histograms demonstrate the distribution of number density with size of the Si nanocrystals, while the FFT pattern demonstrates the corresponding orientations in crystalline planes in the high magnification images [(b) and (d)]. The nc-Si QD in (b) has <220> orientation, whereas, the same in (d) has <111> orientation…………………………………………………………………………………………………………………….. 216

**Figure 8.6:** A typical survey scan XPS spectrum of the sample at \( p = 10 \) mTorr. The insets shows the narrow scan XPS spectra of the N 1s………………………………………………………….. 217

**Figure 8.7:** Room temperature photoluminescence (PL) spectra, under 325 nm excitation by He-Cd laser, of nc-Si/a-SiN\(_{x}\):H QDs thin films deposited by ICP-CVD at different pressures, \( p \)…………………………………………………………………………………………………………………….. 219

**Figure 8.8:** Band gap widening on reduction in the size of nc-Si QDs. Data: (pink circle) obtained from PL peak position 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…………………………………………………………………………………………………………………….. 220