Synopsis
Materials at nanoscale show unique properties due to their large surface-to-volume ratio and or quantum size effects. In addition, studies at nanoscale are important for miniaturization of devices with improved performances. Recently, there have been large number of studies on a new class of materials - known as nanocomposites (NCps) in which nanostructures are embedded into a processable matrix that can be either ceramic or polymer [1,2]. These NCps find applications in variety of devices e.g. photovoltaic [3,4], optoelectronic [5], etc. It is therefore essential to synthesize and characterize the NCps, to ensure the reproducibility of the process that can be scaled-up. The properties of NCps depend not only on the individual components, but also on their interaction and morphology [2]. Therefore, to have desired control on growth of a NCp, it is imperative to understand the characteristic of individual component in the presence of other and the formation mechanism(s) of NCps. Raman spectroscopy is an excellent non-contact, non-destructive optical tool to study size, crystalline quality, stress, surface/interface, structure, phase transition, effect of doping etc. of a semiconductor nanostructure. Therefore, spatial variation of local bonding environment of semiconductor nanocrystals (NCs) in a matrix can be effectively probed using Raman mapping.

The motivation of this thesis work was to use Raman spectroscopy for the investigation of two specially chosen class of NCps: (i) Si-SiO$_2$ (ceramic matrix) and ii) CdS-polyvinyl pyrrolidone (PVP: polymer matrix) NCps. In the first case, an inorganic ceramic matrix is an oxide of the same semiconductor, whereas in the second case, organic matrix provides a completely heterogeneous NCp. The interactions between the semiconductor NCs and a matrix are expected to be quite different in these two cases. The results obtained using Raman spectroscopy had been supported by other techniques, such as, atomic force microscopy (AFM),
X-ray diffraction and X-ray photoelectron spectroscopy (XPS).

This thesis is organized into five chapters.

Chapter 1: Introduction

In this chapter, we begin with a brief history of semiconductors and its ever increasing presence in various fields [3-5] like electronics, optoelectronics, photovoltaics, etc. The importance of semiconductor NCs and the relevance of semiconductor NCps are discussed. A brief overview of the literature on some special class of NCps is presented. In particular, Si-SiO$_2$ (semiconductor-semiconductor oxide) and CdS-PVP (inorganic-organic) NCps are discussed in detail. Use of Raman spectroscopy/mapping, which is our main research tool to study both the NCps, is described. Finally, the motivation of the thesis work is presented.

Chapter 2: Experimental techniques

This chapter describes experimental techniques used for the study of Si-SiO$_2$ and CdS-PVP NCps. Si-SiO$_2$ single and multilayer NCps were grown on crystalline Al$_2$O$_3$ substrate using pulsed laser deposition (PLD). Si and SiO$_2$ targets were ablated alternatively in the chamber by varying the deposition time of silicon, while keeping the SiO$_2$ deposition time constant. CdS-PVP NCps were grown on glass substrate using chemical bath deposition. The bath parameters like concentration of Cadmium acetate (Cd ion source: Cd-A), Thiourea (S ion source: ThU) and PVP, deposition time, heating/cooling cycles were varied to study growth of this NCp.

Working principles of Raman spectroscopy/mapping and AFM are presented. Theoretical background for Raman spectroscopy is also discussed. Basic optical techniques like absorption, photoluminescence and diffuse reflectance spectroscopy, which were used to get information about band gap, are described. X-ray diffraction (XRD), XPS and electron microscopies like scanning electron microscopy (SEM), transmission electron microscopy (TEM) and its variants
are also described.

Chapter 3: Si-SiO$_2$ nanocomposites

In Si-SiO$_2$ NCps, large variation in Si optical phonon from 495 - 519 cm$^{-1}$ has been reported over a decade in different NCps [6-8]. In this Chapter, Raman mapping of Si-SiO$_2$ NCps grown using PLD, was used to elucidate the origin of this variation reported in literature and also observed by us in each of these NCps. This allowed us to perform systematic investigation of the whole range of Si phonon frequencies under same experimental conditions. Raman spectroscopy monitored local laser irradiation experiment was performed on desired frequencies located using Raman mapping. In this five step experiment, changes in Raman spectra were measured, while laser irradiation was kept ON and OFF for certain durations. The understanding developed along with Raman and AFM mapping on same sites were further used to get unique information about the morphology of these NCps grown using PLD.

i) Correlation of size and oxygen bonding at the surface/interface of Si nanocrystals in Si-SiO$_2$ nanocomposites

Based on the difference in line shapes of Si phonons and their behavior during the laser irradiation experiment, low frequency (LF: 495 - 510 cm$^{-1}$) and high frequency (HF: 515 - 519 cm$^{-1}$) phonons were attributed to the surface/interface of Si NCs and SiO$_2$ matrix and core of Si NCs, respectively. Unusual Stokes/anti-Stokes Raman intensity ratio for LF phonons indicated that LF phonons may be observable due to resonance enhancement of Raman signal. This understanding was also found to be consistent with the observation of such a strong signal coming from surface/interface of Si NCs in Si-SiO$_2$ NCp. Density functional and time dependent density functional theory based calculations of Raman spectra (C. Kamal, ISUD, RRCAT) for Si cluster (Si$_{41}$) terminated by oxygen (Si$_{41}$O$_{42}$H$_{24}$) had shown strongest Raman mode $\sim$512 cm$^{-1}$ to
be originating from vibrations of surface atoms. This can be considered to be analogous to LF phonons. Further, XPS measurements of two Si-SiO$_2$ NCps containing contrasting content of LF phonons, was well corroborated with the observation of LF phonons from smaller size Si NCs. With the understanding that LF and HF phonons originate at surface (smaller size) and core (larger size) of Si NCs, respectively, origin of intermediate frequency (IF: 511 - 514 cm$^{-1}$) phonons is discussed in the next section.

ii) Resonance Raman mapping of Si-SiO$_2$ nanocomposite: Monitoring and manipulation of Si nanocrystals

Mainly two types of IF phonons, IF1 and IF2 with very different asymmetric line shape as well as intensities were observed in Raman mapping. It was found that both IF phonons can be explained using superposition of LF and HF phonons, considering that these phonons originate from intermediate size Si NCs and thus have contributions from both surface/interface and core phonons in different proportion. Observed blue shift and increase and decrease in the intensity for IF1 and IF2 phonons during the laser irradiation experiment can both be correlated to increase in size of Si NC and thereby leading to a dominant contribution of core phonons. Further, Stokes/anti-Stokes Raman measurements in corroboration with results of wavelength dependent Raman mapping showed that resonance Raman scattering is crucial for the observance of surface/interface phonons. These results were further supported using absorption spectroscopy. It is also important to note that during laser irradiation at low power, we found that if enough time is given, Si NCs grow in size to give larger core phonon contribution i.e. LF phonon gets converted to IF phonon and IF phonons gets converted to HF phonon further confirming our attributions of these phonons. This can allow Raman spectroscopy monitored, controlled manipulation of the Si-SiO$_2$ device properties using laser.
The correlation of our understanding and data from literature showed that LF, IF and HF phonons originate from smaller size (< ~ 4 nm), intermediate size (~ 4 nm to ~ 6 nm) and larger size (> ~ 6 nm) Si NCs, respectively. Further, we established that resonance Raman scattering is crucial for the observance of surface/interface phonons. Thus, occurrence of surface/interface phonons depends on two factors 1) size of Si NC (optical band gap) and 2) excitation wavelength. This study showed that the effect of surface/interface for Si NCs is due to interaction of surface atoms of Si NC with Si and Oxygen atoms in the matrix. Our study, thus explained the variation of Raman data reported in the literature over the years for Si-SiO$_2$ NCps. Further, presence of multiple optical gaps in Si-SiO$_2$ NCps makes it a good candidate for third generation photovoltaic devices. Our understanding developed for Si-SiO$_2$ NCp can be gainfully used to manipulate and characterize the NCp, simultaneously for photovoltaic device applications using laser.

iii) **Understanding the morphology of nanocomposites from correlation of Raman and AFM mapping**

Raman and AFM mapping together showed formation of clusters of Si NCs embedded in SiO$_2$, although the growth was carried out to be multilayer. Further, Raman mapping showed two types of clusters with i) Gaussian and ii) non Gaussian intensity patterns of Si phonons. Correlation of phonon intensity patterns with observed AFM data on the same selected area, indicated that clusters of Si NCs, small in size ~ 100 nm (organized in two dimension) and large in size ~ 2 µm (three dimension (3D)) are formed. Further, Raman mapping performed with varying focal spot along the depth confirmed this observation and revealed that some of the 3D clusters are stacked with smaller Si NCs at the top and larger Si NCs at the bottom. Raman and AFM mapping of a single layer indicated that Si NCs are formed in the plume itself and cluster
formation occurs by rupturing SiO\textsubscript{2} buffer layer. Annealing at 800 °C in Si rich SiO\textsubscript{2} was found to be the cause of stacking of smallest size Si NCs at the top layer of the cluster. Thus, understanding of Si phonons in SiO\textsubscript{2} matrix led to an important information of the morphology and thereby growth mechanism of Si-SiO\textsubscript{2} NCps, which was difficult to obtain by any other conventional technique.

iv) **Size dependent interface bonding of Si nanocrystals in Si-SiO\textsubscript{2} nanocomposite: corroboration of Raman and XPS study**

In the previous sections, we have discussed the use of Raman mapping to study surface/interface of Si-SiO\textsubscript{2} NCps. In this section, we discuss one to one corroboration between size dependence of surface/interface of Si-SiO\textsubscript{2} NCps using Raman mapping and XPS. The beam size in XPS (~ 1 cm x 1 cm) covers the full NCp; therefore, an average signal from XPS measurement needs to be corroborated with the statistical information obtained from the Raman data. XPS measurements showed observance of Si\textsuperscript{1+}, Si\textsuperscript{2+} and Si\textsuperscript{3+} suboxide states with higher intensity in the NCps corresponding to higher content of HF, IF and LF phonons in Raman mapping, respectively. Thus, quantitative corroboration between Raman mapping and XPS had been established for all NCps studied. Observed one to one corroboration was understood as due to formation of smaller Si NCs in Si excess SiO\textsubscript{2} (top layer) during annealing at 800 °C.

**Chapter 4: CdS-PVP nanocomposites**

CdS-PVP NCps was chosen to study, as monomers of PVP prefers to complex with many inorganic compounds and thus provide surface passivation. In the literature, most of the reports showed that CdS-PVP NCps are grown using two-step growth processes, wherein NCs capped with polymer are grown separately and are incorporated in polymer matrix [9-11]. We had
chosen one-step growth process, wherein CdS NCs and PVP matrix were being grown simultaneously using chemical bath deposition (CBD).

i) Insight into one-step growth of nearly monodispersive CdS nanocrystals embedded in polyvinyl pyrrolidone spheres

In this section, we discuss the optimization study of CdS NCs embedded in PVP, grown using one-step CBD. Systematic study of variation in Cadmium acetate (Cd ion source: Cd-A), Thiourea (S ion source: ThU) and PVP concentration, deposition time, heating/cooling cycles; elucidated co-operative growth mechanism for CdS-PVP NCp. This results in different optimum growth conditions for the formation of CdS-PVP NCp than that for CdS thin film. Absorption, scanning and transmission electron microscopy together, showed that nearly monodispersive CdS NCs with sizes ~ 6 to 10 nm for different NCps are embedded in PVP sphere (sizes ~ 100 - 900 nm). Diffuse reflectance spectra was used as a guide to separate scattering contribution from absorption spectra. The scattering contribution was understood to be occurring due to Rayleigh and Mie scattering due to PVP spheres/structures seen in SEM micrographs. Our observations and understanding suggested that formation of PVP spheres led to inclusion of nearly monodispersive CdS NCs with better passivation. Further, decrease in size of CdS NCs with higher molar concentration of Cd-A & ThU and formation of nearly monodispersive CdS NCs embedded in PVP spheres were corroborated qualitatively with existing growth modeling studies of NCps. Co-operative nature of growth for CdS-PVP NCp using CBD was further investigated using Raman and AFM mapping.
ii) Effect of relative concentration of Cd/S ion source and PVP content on the morphology of CdS-PVP nanocomposite: Raman, PL and AFM mapping study

Raman and AFM mapping investigation of CdS-PVP NCps on same selected sites showed two different morphologies of CdS-PVP NCps, wherein CdS NCs are embedded in i) PVP sphere and ii) thin film of PVP for different relative concentration of Cd-A/ThU to PVP, as a result of co-operative growth mechanism. It has been predicted that the morphology depends on the density of NCs, if the strength of interaction is same [12]. We found that larger concentration of Cd/S ion source (larger density of CdS NCs) led to formation of PVP sphere, whereas, thin film of PVP was observed in case of lower concentration of Cd/S ion source, which is consistent with the theoretical prediction [12]. Further, formation of PVP spheres led to inclusion of nearly monodispersive CdS NCs of better crystalline quality. In addition, we found that smaller CdS NCs of better crystalline quality with better passivation were embedded in smaller PVP spheres, which was found to be a minimum energy configuration [13].

iii) Effect of growth temperature on the morphology of CdS - PVP nanocomposites: Raman and AFM mapping with XRD

Three dimensional intensity profile in Raman image of isolated PVP sphere indicated volume absorption of CdS NCs, which is driven by attractive interaction between NCs-polymer and high density of NCs, leading to the collapse of polymer [13]. Further, it was found that this collapse transition of PVP is not favored at 70 °C and thus it led to opening (at 70 °C) and reformation (room temperature) of CdS-PVP NCp. Grazing incidence XRD (INDUS, BL-12) data showed formation of both cubic and hexagonal phases for NCps grown at room temperature, whereas, chemical bath heated at 70 °C leads to NCps with purely hexagonal phase. Further, Raman, PL and AFM mapping in corroboration with XRD data showed that there exist
residual tensile stress in CdS NCs embedded in single PVP sphere as compared to the dimer, which led to observance of resonance Raman scattering of CdS NCs due to stress related band gap tuning.

To summarize, one-step growth of CdS-PVP NCp using CBD was found to be co-operative in nature. While, this method eliminates an additional step for growth of NCps, we found that complexity of the process actually led to better control on the growth i.e. formation of nearly monodisperse CdS NCs of better crystalline quality and with better passivation. This is expected to enhance the non-linear optical properties of CdS NCs, which are useful for optical limiting devices.

Chapter 5: Conclusion

This chapter summarizes results of work presented in the earlier chapters. In Si-SiO$_2$ nanocomposites grown by pulsed laser deposition, large variation (495 - 519 cm$^{-1}$) in Si phonon frequencies was shown to arise from surface/interface of smaller Si nanocrystal and core of larger Si nanocrystals dispersed in SiO$_2$ matrix. The large size distribution of Si nanocrystals in these nanocomposites was used advantageously to probe similarity and differences in them under certain experimental conditions. This Raman spectroscopy/mapping study showed that the extended interface generated due to interaction between surface atoms of Si NC and Oxygen in the matrix plays an important role in Raman spectra, contribution of which depends on the size of a Si nanocrystal. Further, it was found that the resonance Raman scattering is crucial for the observance of these surface/interface phonons. This understanding can now be well correlated to variation of Si optical phonon frequency reported in literature. Further, this understanding in corroboration with atomic force microscopy revealed stacking of different size Si nanocrystals in clusters of Si-SiO$_2$. This unique information about morphology of Si nanocrystals embedded in
SiO$_2$ is difficult to obtain by any other conventional technique. Similarly, in CdS-PVP nanocomposites grown using chemical bath deposition, the interaction between CdS nanocrystal surface and PVP monomers gave rise to collapse of polymer, which in turn led to formation of nearly monodispersive CdS nanocrystals embedded in PVP spheres. The complexity of one-step growth process actually allowed desired control on growth of CdS-PVP nanocomposite using a simple growth technique of chemical bath deposition.

In both nanocomposites studied, it was found that interaction between constituent parts i.e. semiconductor nanocrystal and matrix plays an important role in determining the morphology as well as properties of nanocomposites. The Chapter is concluded by bringing out the future scope of work.

References