RAMAN AND PHOTOLUMINESCENCE SPECTROSCOPY OF SILICON NANOSTRUCTURES

by

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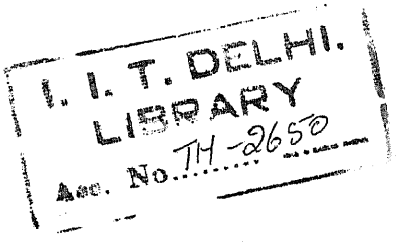

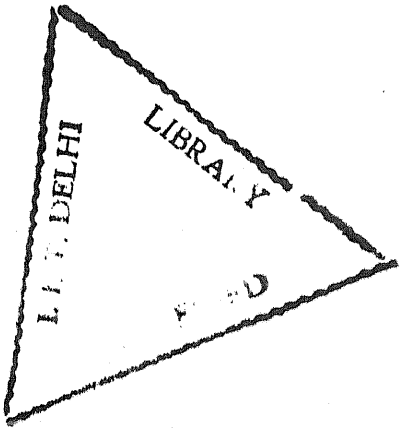

DEDICATED TO MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled "**RAMAN AND PHOTOLUMINESCENCE SPECTROSCOPY OF SILICON NANOSTRUCTURES**", being submitted by **Puspashree Mishra** for the award of the degree of Doctor of Philosophy, to the Indian Institute of Technology, Delhi, is a record of bonafide research work she has carried out under my guidance and supervision.

In my opinion, this thesis has reached the standard fulfilling the requirements of all regulations relating to the degree. The results contained in this thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

K P Jain

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Prof. K. P. Jain

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ABSTRACT

Quantum confinement effects in low dimensional semiconductor systems offer great deal of flexibility in tailoring the electronic and optical properties and thus these systems are potential candidates for future electronic and optoelectronic devices. Bulk silicon is the dominant material in the microelectronics industry. However, it is an inefficient light emitter being an indirect band gap material and consequently its role is limited in optoelectronics. The recent discovery of strong room temperature luminescence from silicon nanocrystals fabricated by different methods is an extremely important scientific breakthrough with enormous technological implications because of possibility of integration of silicon based electronic and optoelectronic devices. The photoluminescence process from these materials remains controversial despite several experimental and theoretical studies.

Reduced dimensionality results in perturbations in the crystal potential and thus both the vibrational and electronic properties are modified. Confinement of electrons and other elementary excitations in nanometer size crystals is sensitive not only to the physical dimension but also to the shape. The existence of a large surface to volume ratio in small size crystals and a large size distribution of crystallites in samples formed by conventional growth processes further alters and complicates the properties. Raman, photoluminescence and absorption spectroscopy are powerful non-destructive optical tools to study these changes.

This thesis aims at understanding the effects of confinement on the electronic properties, vibrational properties and the luminescence process in silicon nanocrystallites. The effects of growth parameters and the surface conditions on the overall properties of the nanocrystallites have also been investigated. Two different class of nanocrystallites such as the silicon nanocrystallites embedded in the a-Si:H matrix formed by CW laser annealing process and silicon nanocrystallites in SiO_2 matrix produced by rf cosputtering process have been chosen for the above study. Room temperature Raman experiments were performed in order to investigate the effects of reduced size on the first order and the higher order modes in

nanocrystals. Temperature dependent Raman studies on CW laser annealed samples gave important information regarding finite size effects, anharmonicity and phonon life times. We performed resonant Raman experiments on the CW laser annealed nanocrystals in order to study the influence of quantum confinement on the electronic structure. Luminescence mechanism in CW laser annealed samples was understood based on room temperature and temperature dependent photoluminescence experiments. Finally, detailed room temperature and temperature dependent photoluminescence studies and absorption studies on the Si doped SiO_2 samples enabled us to understand the importance of the quantum confinement and the surface localized states in the luminescence process.

Stable silicon nanocrystals of average dimensions in the range 2 - 7 nm were fabricated by controlled CW laser annealing of a-Si:H with proper optimization of the annealing power density, exposure time and the scan speed of the annealing beam. Two different samples of a-Si:H of thickness 5000 Å and 1100 Å were used to study the thickness dependence of the formation of nanocrystals and the annealing process. The average dimension of nanocrystals was determined by a detailed line shape fitting process of the first order phonon to a phenomenological model. The contribution from the amorphous component and the interfacial strain due to different thermal expansion coefficient of the film and the substrate has been discussed. The effects of reduced dimensionality on the first order and the higher order modes have been analyzed in detail.

The peak width and the peak position of the first order phonon in the CW laser annealed nanocrystals were found to vary with the change in temperature. These changes are attributed to the anharmonicity in the vibrational potential. Finite size effects provide additional temperature insensitive broadening and shift of the phonon. The anharmonic constants related to the peak position and peak width are found to be opposite in sign. The degree of anharmonicity increases asymptotically with decreasing size of nanocrystals. The anharmonic constants related to the intrinsic width and the additional width due to finite size effects are size dependent and increase asymptotically with decreasing size. The constant related to the additional width due to finite size effects changes more rapidly compared to the constant related to the intrinsic width.

The intrinsic phonon life time related reciprocally to the intrinsic width decreases with

increasing temperature due to greater thermal interaction at higher temperatures. There is also an increase in the phonon decay rate due to finite size effects. The intrinsic phonon life time and the finite boundary related lifetime decrease with decreasing size, the change being more rapid for finite boundary related lifetime. Phonons decay mainly via the intrinsic path for large crystals while the decay at the finite boundary becomes more pronounced in smaller crystals.

The resonance behavior in CW laser annealed samples in the energy range 2.41 eV - 2.71 eV was studied. A variation in the shape of the first order mode in case of nanocrystals of small average dimensions was attributed to selective excitation of nanocrystals of a certain size distribution. No such change in case of large crystals was found confirming weak nature of confinement in large crystals. Resonance behavior of higher order modes showed similarity between the 2TO mode of the bulk and the nanocrystals while the 2LO mode showed exactly the opposite trend.

Weak and two peaked luminescence was detected in the orange region of the visible spectrum from the CW laser annealed samples. The PL peak positions were insensitive to the size of the nanocrystals and the PL intensity was found to be strongly dependent on the annealing power density and atmospheric storage. The temperature dependence of the PL intensity and the position was found to be anomalous. The luminescence process was attributed to the surface localized states.

In order to study the production process dependence of the nanostructure properties, Raman, photoluminescence and absorption experiments on Si nanocrystals in SiO_2 matrices prepared by rf sputtering process and annealed in argon atmosphere at different temperature and for different durations were carried out. The room temperature Raman experiments reveals that larger nanocrystals are formed for the samples with largest Si/SiO_2 compositional fraction and the dimension of the nanocrystals increase with increasing annealing temperature and duration. Raman results also indicate a threshold annealing temperature for the formation of nanocrystallites.

Absorption experiments support the Raman results and the quantum confinement effect in nanocrystallites, thus showing a higher blue shift of the absorption edge for smaller size nanocrystals. The exponential behavior of the absorption coefficient in the energy range 1.7 eV -

3.1 eV with a large *Urbach* energy suggests large distribution of particle size, variation of the surface conditions and the variation of the oscillator strength with size. Higher blue shift in the as deposited films as compared to the annealed films suggests the presence of very small Si clusters in the as deposited films.

The PL from these samples are broad with FWHM in the range of 300 - 550 meV and are in the visible region. The average dimension of nanocrystals was calculated from a line shape fitting procedure of the PL using a phenomenological model and showed disagreement with the Raman result. The temperature dependent PL results are anomalous and are found to be dependent on a competition between the radiative and nonradiative process.

The above results are analyzed in terms of a combination of radiative recombination of carriers in the crystalline core and the interfacial region between the core and the SiO_2 matrix. The band gap of the interfacial layer varies with the O_2 covering ratio and the band gap of the core varies with the dimension of the crystalline core. The recombination of the carriers occurs either in the core or in the interface depending on the relative band gaps. All experimental results could be explained on the basis of the combination of these two models. The extra sensitiveness of the PL peak position, intensity and the shape to atmospheric storage further supports the involvement of the surface localized states in the luminescence process.

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