Chapter 6

Conclusions and Suggestions For Future Work

6.1 Conclusions

In this work, there have two major studies focused on the growth and characterization of hydrogenated silicon (Si:H) thin films by layer-by-layer (LBL) deposition technique using radio-frequency (rf) plasma enhanced chemical vapour deposition (PECVD) system have been carried out successfully. The first study was the deposition of Si:H thin films by continuous deposition (CD) and LBL deposition at various deposition conditions of rf power, substrate temperature and hydrogen to silane flow-rate ratio. The influence of these deposition conditions on the optical and structural properties of the films deposited by LBL and CD techniques are analyzed and compared. The optical properties such as film thickness, refractive index and optical energy gap were determined from the optical transmission spectra of the films deposited on glass substrates measured using ultra-violet visible near-infrared (UV-VIS-NIR) spectroscopy technique. The FTIR transmission spectra were carried out on films deposited on c-Si substrates to study the silicon bonding configurations present in the films. The XRD characterization technique was used to observe evidence of crystallinity in the films deposited on both c-Si and glass substrates. The influence of substrate on the crystallinity for LBL and CD deposited films were compared.

The second study was focused on the structural properties of hydrogenated nanocrystalline silicon (nc-Si:H) thin films deposited on c-Si substrates by LBL deposition technique at the different deposition conditions which were shown to have crystalline structures. This study was concentrated on the morphology, crystallinity, crystallite size and silicon-oxygen bonding properties of this material in relation to the deposition parameters. The relation between these properties to the PL emission properties of the films was studied and a model for the deposition mechanism and structure of the nc-Si:H films deposited by LBL technique was proposed. In this study, the FTIR data obtained in the first study was used to investigate the silicon-oxygen bonding properties which were shown to have strong influence on the PL properties. The XRD data from the first study was also used to determine crystalline volume fraction and crystallite size of the Si grains. Micro-Raman scattering spectroscopy, field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscope (HRTEM) were used to correlate the various crystallite and grain sizes obtained from these measurements and also XRD measurements.

6.2 Important Results

Based on the results in the first part of this work, it was established that rf power and substrate temperature produced significant changes to the optical and structural properties of the LBL films compared to the CD films. The periodic hydrogen plasma treatment on the growth surface of the film was the key factor in the LBL deposition process which contributed to the effective control of the electro-optical properties namely film thickness, optical energy gap, refractive index and crystallinity in the film structure. The optical transmission spectra of the films established that Si:H films grown by LBL deposition are of mixed phases of amorphous and nc-Si. The substrate temperature was shown to have the most significant influence on the phase structure of these films. In CD growth, plasma has significant influence on nucleation because growth and nucleation takes place at the same time at the growth surface. Nucleation does not depend critically on the plasma properties during the deposition process in LBL growth since nucleation is mainly induced by the hydrogen plasma treatment. These factors produced the reversed trends of the growth rate with respect to rf power and substrate temperature for these Si:H films deposited by the LBL and CD deposition techniques using rf PECVD. The deposition rate of LBL deposited Si:H films decreased with increase in rf power and increased with increase in substrate temperature and vice-versa for the CD deposited films.

The substrate temperature was shown to produce the significant effects on the refractive indices of the Si:H films grown by LBL technique. The refractive index of films is usually related to the compactness and density in the film structure. The increase in substrate temperature increased the thermal annealing effect of the growth surface during the hydrogen plasma treatment of the LBL film and this contributed to a more compact film structure as indicated by the increase in refractive index of the films. However, high substrate temperature of 400°C retarded the increasing of refractive index due to evolution of hydrogen. This increases in the number of dangling bonds which resulted in the formation of voids in the film structure thus forming a less dense film structure. The optical energy gap and the hydrogen content were strongly dependent on substrate temperature in LBL films. Even though the substrate temperature also showed significant influence on the hydrogen content in CD films but the rate of change was larger for the LBL films. The periodic hydrogen plasma treatment in the LBL process enhanced the removal of hydrogen from the Si:H film structure at high substrate temperatures and this significantly reduced the optical energy gap. The presence of Si nano-crystallites (~ 2 nm) and the high crystalline volume fraction (X_C ~ 41-54 %) of these films contributed to large optical energy gaps of the LBL films deposited at 100 and 200°C revealing that quantum confinement effects played a significant role in the broadening of the band gaps of these films.

The increase in ion bombardment effects with increase in rf power increased the disorder in the structure of the Si:H film deposited by CD method but the periodic hydrogen plasma treatment in the LBL deposition process was shown to be effective in annulling the destructive effects of the ion bombardments. The structural disorder for the LBL films were always much lower than the CD films at all deposition parameters showing that LBL process improved structural order and high substrate temperatures were most effective in increasing the structural order of the films. The films deposited on c-Si substrates were crystalline while the films on glass substrates were mostly amorphous.

The results in phase two of this work revealed that the lattices of c-Si (111) substrates acted as a seeding layer inducing the formation of nc-Si structures especially for the LBL films. The periodic hydrogen plasma treatment on the film surface further enhanced the crystallinity of the LBL films. Increase in rf power produced a change in the preferred orientation plane from (311) to (111) with increase in rf power for both CD and LBL films. The change in the preferred orientation increased structural disorder in CD films but showed very little effect on the structure of the LBL films.

The second study of this work involved detailed analysis of the XRD, Micro-Raman scattering spectroscopy, FESEM and HRTEM results. The results produced inconsistent trends and sizes with respect to the crystallite sizes measured from samples deposited at various substrate temperatures and rf powers. From detailed analysis of these data it was revealed that the LBL deposition process actually resulted in the formation two distinct layers of low dimensional Si:H nano-structures on c-Si (111) substrates. The region directly above the c-Si substrate was covered with a layer of nc-Si:H film. The growth of this film was induced by the lattices in the (311) orientation plane of the substrate which acted as a seeding layer. Larger nano-crystallites with preferential orientation along the (311) plane were formed in these lower layers. Aggregates of nc-Si grains were formed in the upper layers when the growth induced by the seeding layer was reduced. The nc-Si grains consisted of Si nano-crystallites embedded in an amorphous matrix.

It was revealed that crystallinity and crystallite sizes played an important role in the PL emission properties of the films. The PL emission produced by the LBL films was produced mainly by the nc-Si grains in the upper layers. The LBL deposition process was capable of forming nc-Si grains consisting of Si nano-crystallites embedded in mixed phases of amorphous silicon (a-Si) and amorphous silicon oxide (a-SiO) matrix, and the proportion of these phases in the grain boundary was dependent on the substrate temperature. The presence of a-SiO phase in the grain boundaries enhances quantum confinement effects and the formation of highly crystalline grains produced high intensity PL emission at room temperature. The ten minutes hydrogen plasma treatment on the c-Si substrate prior to deposition done was shown responsible for the incorporation of O into the amorphous phase of the nc-Si grains. The growth of the earlier layers was induced by the exposure of the Si (311) lattice to the hydrogen plasma treatment. These lattices acted as seeding layers for the growth of the nc-Si:H film with preferred orientation along the Si (111) plane. The initial hydrogen plasma treatment produced sufficient thermal energy to weaken Si-O bonds and diffused the O atoms upwards through the nc-Si:H film layer during the subsequent growth process. When the effects of the seeding layer of the c-Si lattice diminished as the nc-Si:H layer increased in thickness, nc-Si grains were formed instead and some of these O atoms were then absorbed into the amorphous matrix of the grains. Based on these results, the growth mechanism of nc-Si grains has been proposed to explain the formation of nc-Si grains consisting of Si nano-crystallites embedded in mixed phases of a-Si and a-SiO matrix which has capable in producing high intensity of PL emission.

The results in this work have shown that LBL deposition process using rf-PECVD whereby alternate hydrogen plasma treatment and growth process were repeated periodically was successful in the growth of nc-Si grains with light emission properties. The crystallite size, crystalline volume fraction and the fraction of a-SiO in the grain boundary of the nc-Si grains can be controlled by rf-power and substrate temperatures. These parameters influenced the PL emission properties of the nc-Si grains. These nc-Si:H grains with high surface to volume ratio and tunable PL emission properties can be useful in bio/bio-chemical sensor applications.

From the summary of the important results, the objectives of the work have been successfully achieved. The firstly completed with the detail investigations and comparison on of the properties of the films deposited by CD and LBL at different optimized deposition conditions. The influence of the substrates on the crystallinity of the films has been succeffully verified. The morphology, crystallinity, crystallite size and silicon-oxygen bonding properties of the films deposited on c-Si substrate by the LBL have been further investigated and studied. Finally, these properties of the films have been succefully explained the PL emission properties of the Si nanostructures. Last and not least, growth mechanism of the Si nanostructures by LBL deposition has been successfully proposed based on the conclusive results and discussions of the properties of the films.

6.3 Suggestions for Future Work

In conclusion, it can be stated that LBL deposition process using rf-PECVD is a very promising technique for the growth of nc-Si grains with light emission properties. However, much work is still needed to obtain precise control the crystallite size, crystalline volume fraction and the fraction of amorphous SiO in the grain boundary in order to enhance the PL emission properties of the nc-Si grains. Deposition pressure is another important deposition parameter in controlling the crystallinity of the material. Thus, the study of the effect of deposition pressure is needed in order to optimize the PL emission intensity of these Si nanostrucutures.

In-situ gas-phase diagnostics techniques such as optical emission spectroscopy (OES), mass spectroscopy and diode laser absorption (DLA) which enables measurements of the density of reactive species in the steady state of plasma to strengthen the existing model on the growth kinetics of this material. The concentration of emissive and ionic species of such as SiH_3, SiH_2, SiH, Si and H measured during the various phase of the growth process with respect to the studied deposition parameters determined from this measurement will enable precise control of the parameters required for tunable PL emission properties for useful applications of these nc-Si grains.

A more detailed study using the HRTEM can confirm the configuration of the structure of the material as proposed by the growth mechanism model. Energy dispersive X-Ray spectroscopy (EDX) analysis using the HRTEM can confirm the components of the nc-Si grains grown at different rf-power and substrate temperatures. Selected area diffraction spectroscopy (SAED) analysis can confirm the lattice structures of the nc-Si:H film layer above the substrate and the nc-Si grains above this layer.

More variations in the growth parameters would help shed more light on the required parameters to enhance the PL emission properties for useful application of these nc-Si grains. Application of these nc-Si grains as bio/ bio-chemical sensors and gas sensors can be tested with respect to the structural properties of the grains grown.