Growth and characterization of amorphous Si based multilayer structures

Kamyab, Lobna

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Growth and Characterization of Amorphous Si based Multilayer Structures

Lobna Kamyab

School of Electrical & Electronic Engineering

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I dedicate this thesis to the most astonishing person I have ever known, my mother Pourandokht Kamyab.

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Abstract

Silicon is a widely available material with very good electrical, thermal and mechanical properties suitable for the manufacture of electronic devices and has contributed to the big success of microelectronics. The trend in Si microelectronics towards faster and smaller devices has resulted in many issues such as heat dissipation, crosstalk and RC delay in metal interconnects. To address these issues while achieving faster inter-component communication and keeping the costs low, Si microphotonics which focuses on the development of Si based photonics devices has been actively pursued. To date almost all Si based optoelectronic components, such as waveguides, detectors and modulators have been realized except for an efficient light source. Many attempts have been made to obtain visible light emission from Si utilizing amorphous Si (a-Si) and/or Si nanostructures. These include porous Si, Si nanocrystals embedded in a dielectric matrix. Another approach to based low dimensional Si based materials to achieve light emission, is to utilize multilayer structures. These structures have the advantages of reproducibility and thickness controllability, which makes them leading competitors in this field.

In this work we have fabricated a-SiN_x:H/SiO₂ multilayer quantum well structures consisting of 20 alternating layers of a-SiN_x:H and SiO₂ using the plasma enhanced chemical vapor deposition (PECVD) technique. a-SiN_x:H has been chosen as it is an efficient light emitting material and its bandgap can be tuned in a wide energy range. This property will give rise to greater flexibility in controlling and optimizing the emission characteristics. With the prospect of optimizing the N content in our a-SiN_x:H material for its light emission we have started with studying single layer a-SiN_x:H material. They have been grown by varying the Si source gas (SiH₄) and N source gas (NH₃) flow ratio in the range of 1.05 to 3.16. Their

optical properties, including the bandgap, Urbach energy and complex refractive indices were obtained by a detailed study of their spectroscopic ellipsometry data. The optimum gas flow ratio for efficient light emission was found to be 1.58.

The multilayers consist of 20 alternating layers of a-SiN_x:H material as the well and SiO₂ as the barrier layers. The growth condition for a-SiN_x:H well layer was chosen to be the same as the sample with gas flow ratio of 1.58, since it was found to be the optimum condition for PL efficiency. The SiO₂ barrier layer were grown using N₂O and SiH₄ as O and Si source gases. To study the effect of well layer thickness, two different multilayer structures with fixed barrier layers of 10 nm and well layer thicknesses of 3 and 6 nm were fabricated. The complex refractive index of the a-SiN_x:H well layers and SiO₂ barrier layers were determined from SE data fitted to a model utilizing Tauc-Lorentz and Cauchy dispersions to describe the well and barrier materials respectively. The layer thicknesses obtained from SE results are in good agreement with the ones measured from TEM graphs.

To achieve a high efficiency EL, we have used a structure where electric current is injected laterally and parallel to the multilayer structure. In this way, the current mainly flows only through the well layers and not the barrier layers, and hence the injection process is expected to be more efficient. In total, 20 layers of alternate a-SiN_x:H well and SiO₂ barrier layers with respective thicknesses of 6 nm and 5 nm were grown. N₂O and SiH₄ were used as the source gases for SiO₂ barrier layer deposition. A post annealing process at 1000°C for one hour in N₂ ambient was performed to enhance the PL intensity. To make the contacts for lateral injection of current, we have etched away the multilayer using reactive ion etching and deposited heavily doped n and p type poly Si on each side of the multilayer structure forming interdigitated contacts. For comparison, a similar multilayer structure has been grown for the fabrication of devices with electric field applied vertically. Heavily n-doped Si substrate and

a 100 nm thick layer of heavily doped p-type poly Si were used as the bottom and top electrodes respectively. The current-voltage relation of the laterally injected PIN structure indicates good rectifying characteristics of the device. A significant improvement of more than nine orders of magnitude has been observed in the laterally injected device as compared to the vertical one. This can be attributed to the absence of highly resistive barrier layers in the current path. We have observed orange color EL from the device under forward bias condition, a result of radiative recombination of electron hole pairs injected from the n and p poly Si.

List of Abbreviations

2D: Two Dimensional

3D: Three Dimensional

a-SiC:H: Hydrogenated amorphous Silicon Carbide

a-SiN_x:H: Hydrogenated amorphous Silicon Nitride

c-Si: Crystalline Si

CLU: Cody-Lorentz-Urbach

CMOS: Complementary Metal Oxide Semiconductor

CVD: Chemical Vapor Deposition

ECR-CVD: Electron Cyclotron Resonance Chemical Vapor Deposition

EL: Electroluminescence

EMA: Effective Medium Approximation

FTIR: Fourier Transform Infrared

HFCVD: Hot Filament Chemical Vapor Deposition

HRTEM: High Resolution Transmission Electron Microscopy

IC: Integrated Circuit

KK: Kramers-Kronig

MSE: Mean Squared Error

PDS: Photothermal Deflection Spectroscopy

PECVD: Plasma Enhanced Chemical Vapor Deposition

PIN: P-type_Intrinsic_N-type

PL: Photoluminescence

PLD: Pulsed Laser Deposition

PMT: Photomultiplier Tube

QD: Quantum Dot

QW: Quantum Well

RF: Radio Frequency

SE: Spectroscopic Ellipsometry

TEM: Transmission Electron Microscopy

TL: Tauc-Lorentz

TLU: Tauc-Lorentz-Urbach

TR: Transmission-Reflection

XPS: X-ray Photoelectron Spectroscopy

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Chapter 1 INTRODUCTION

1.1 Motivation and Background

Silicon (Si) is one of the main factors of the microelectronic's big success since it is a widely available material, easy to manufacture and shows very good thermal, mechanical and electrical properties. The success of Si microelectronics technology has been demonstrated by a dramatic improvement in the performance of integrated circuits without an escalation in the cost. Indeed, a continuous effort to scale down transistors' feature size enables production of smaller and more powerful chips at a lower cost. The increase of transistor density at a pace as predicted by the Moore's law has continued for more than half a century to the present day, as displayed in Fig. 1.1. Nevertheless, as the chips dimensions continue to shrink, heat dissipation problems and speed limitation due to metal interconnects' RC delay have posed serious challenges to the realization of high performance integrated circuits (IC) [2]. The solution for further enhancement of integrated circuits is sought in photonics, which is utilizing photons instead of electrons for data transfer. Chip-to-chip optical instead of electronic communication will not only completely solve the problems concerning the propagation delay, signal interference and heat dissipation in the metal wires, but also provide large information bandwidths [2-5].

Fig 1.1 Historical development of IC transistor counts. The linear fitting shows the accuracy of the Moore's law

The earliest research on optical circuits has been carried out during 1970s and the vision of a chip containing integrated optical components was proposed, as shown in Fig. 1.2. [6]. The integration of Si-based electronics with photonics requires the pursuit of hybrid technologies for light emitters and modulators [7], which are often both expensive and complicated to produce [6]. Study of on-chip optical interconnection on the Si platform was motivated by the dominance of Si as the semiconductor material in microelectronics in the late 1980s [8]. Using the mature Si technology, Si photonics can be integrated with very-large-scale integration electronic circuits in a cost-effective manner on the same chip to provide more functionality [9]. In addition, the well-developed Si processing techniques can be employed in the fabrication of high performance Si-based photonic and optoelectronic devices to reduce the manufacturing cost, if Si photonics is compatible with the mainstream complementary metal-oxide-semiconductor (CMOS) technology. Therefore, Si photonics is attractive and can potentially lead to the realization of monolithic Si optoelectronic IC.

Fig. 1.2 Si-based optoelectronic integrated circuit containing integrated optical components to carry out light generation, modulation, manipulation, detection, and amplification [6]

To date almost all Si photonics components, such as waveguides [10-12], amplifiers [9, 13], detectors [14] and modulators [15-17] have been realized except for an efficient light source [4, 12, 18]. This is because Si is an indirect semiconductor and hence a poor light emitter. The light emission in bulk Si is a phonon-mediated process with a low probability and therefore the non-radiative recombination rates are much higher than radiative ones [19, 20].

Novel strategies are required for Si-based light emitters. The recent report on the first Si-based Raman laser by Intel has stimulated intense interest in Si-based light sources [13]. Although the breakthrough of the Si Raman laser is impressive, such Si lasers are not practical for the on-chip light emitter, because an additional pumping laser is required for the intense optical excitation. Up till now, an all-Si electrically pumped laser is not available, which is one of the major obstacles in the present development of Si photonics.

In order to achieve efficient Si-based light emitters, research on Si or other compatible materials in various approaches has been carried out. One of the most common approaches is using amorphous Si (a-Si) and its alloys [21-35]. Unlike crystalline Si (c-Si), momentum conservation is not obeyed in these materials and radiative recombination can occur efficiently, thanks to the presence of bandtail states [36]. Possible candidates in this category include a-Si [36-39], hydrogenated amorphous Si carbide (a-SiC:H) [21, 23, 24, 33, 40-48] and hydrogenated amorphous Si rich nitride (a-SiN_x:H) [49-55]. The optical properties (e.g. bandgap energy, emission characteristics, complex refractive index etc.) as well as electronic properties (e.g. conductivity and current transport) of these materials are highly dependent on the growth condition and process parameters. However, the very high luminescent efficiency of a-SiN_x:H makes it very attractive amongst other candidates [49-54]. Moreover, compared to a-Si and a-SiC:H for instance, it has a broader range of optical bandgap from 1.9 eV to 5 eV that makes it suitable for obtaining light emission of different wavelengths [29, 31, 32, 34, 49, 56-59].

Apart from amorphous Si based materials, Si nanostructures present another important Si based material for achieving light emission. In 1990 Canham et. al discovered emission of strong visible light from porous Si, which was explained by quantum mechanical effects in Si nanostructures [60-62]. This breakthrough has inspired enormous efforts to exploit low dimensional Si, where one, two or three dimensions of the Si are at the nano scale, to improve the light emission efficiency. For example, Si quantum dots embedded in a SiO₂ matrix have been proposed with enhanced emission efficiency, attributed to the quantum size effect [63, 64]. These structures are advantageous compared to porous Si due to their better stability and full compatibility with Si technology [18]. Although Si quantum dots dispersed in SiO₂ systems have been widely investigated, their recombination mechanism in the blue-violet region is still under debate, and widely believed to be associated with oxygen related defects

or chemical species [65-67]. Controlling the Si nanostructures' surface [68, 69], their size, homogeneity and concentration [66] are important challenges associated with Si quantum dot in SiO₂ matrix which makes it difficult to achieve desirable luminescence properties [54]. With respect to using these structures as electroluminescent devices, the energy barrier between the insulating matrix material and the Si nanostructure becomes an issue. It is difficult to inject electric current efficiently to the light emitting nanostructures through the highly insulating materials such as SiO₂ [50, 70-74]. It has been proposed that materials with lower bandgap such as Si₃N₄, instead of SiO₂, can be used to alleviate current injection issues. However, the potential barrier posed by Si₃N₄ is still substantial for current injection into the Si nanostructures, thus rendering such a system inefficient and not practical for the fabrication of electroluminescent devices.

Another promising solution, which also benefits from the quantum confinement of carriers, is to utilize Si-based multilayer structures [75-82]. Such structures typically comprise a lower bandgap amorphous Si alloy well layers sandwiched by a large bandgap amorphous Si alloy barrier layers. They have the advantages of structural stability compared to other low dimensional systems such as porous Si. Thanks to the advanced deposition technology, quantum well materials with atomic layer precision at the thicknesses required can be fabricated [54]. By controlling the bandgap and/or layer thickness of the well layer in a multilayer structure, the emission wavelength can be tuned due to the quantum confinement effect. This is another major advantage over other structures such as porous Si or Si nanostructures embedded in a dielectric matrix. Moreover, it is possible to efficiently inject electron hole pairs into the luminescent layers in a multilayer structure as the barrier layer is typically very thin in the range of less than 10 nm. This is extremely important towards their application as electroluminescent devices. Therefore, the controllability, uniformity and

reproducibility of multilayer structures, has rendered them one of the leading competitors in the field of low dimensional Si based light emitters [41, 75-78, 83-87].

1.2 Objectives

In this work we propose to study Si rich a-SiN_x:H/SiO₂ multilayer structures to achieve efficient light emitting devices. a-SiN_x:H has been chosen because of its desirable luminescent properties such as high emission efficient and a bandgap that can be tuned over a wide range. SiO₂ was chosen to be the barrier layer material since it has a larger bandgap compared to a-SiN_x:H, and provides a large barrier for the confinement of carriers in the a-SiN_x:H well layer. The objectives of the project include the fabrication of efficient light emitting multilayer structures, the study of their optical properties and emission characteristics, and ultimately the development of multilayer structures light emitting devices using a novel efficient current injection scheme.

With this scope the approach adopted in this thesis is to first grow efficient light emitting a-SiN_x:H materials using plasma enhanced chemical vapor deposition (PECVD) technique. By varying the SiH₄/NH₃ gas flow ratio, a-SiN_x:H with different compositions and consequently varying optical properties and light emitting characteristics can be fabricated. The main objective of this part of our study is to optimize the PECVD deposition conditions for the growth of light emitting a-SiN_x:H material which will be ultimately employed in our multilayer structure. A detailed investigation of this group of material using spectroscopic ellipsometry and photoluminescence (PL) will be carried out to understand their optical and emission properties respectively. An in-depth analysis of the ellipsometry data will be pursued by investigating various optical dispersion models and identifying one that is suitable

for the a-SiN_x:H studied in this work. From this study the complex refractive indices and the thickness of the a-SiN_x:H thin films can be accurately determined. The PL results together with the absorption coefficient obtained from the ellipsometry study is then used to determine the optimum gas flow ratio that will give rise to the most efficient light emitting a-SiN_x:H materials. Following that this optimum condition will be used for the growth of a-SiN_x:H well layers in a-SiN_x:H/SiO₂ multilayer structures. Two different a-SiN_x:H well thicknesses of 3 and 6 nm with a fixed SiO₂ barrier thickness of 10 nm will be fabricated. The evolution of the optical and emission properties of the a-SiN_x:H/SiO₂ multilayer structures with the well layer thickness will be studied in detail. To investigate the optical properties we have chosen spectroscopic ellipsometry technique due to its very high accuracy and extreme sensitivity to very thin layers. The ellipsometry data analysis for structures consisting of many thin layers is however a great challenge. Previous report on ellipsometry characterization of multilayers is limited to investigation of only the layer thickness but not the complex refractive indices [88]. Therefore, one of the main objectives of this work is to characterize the optical properties of such multilayer structures accurately using spectroscopic ellipsometry. Finally, we use the optimum deposition condition to fabricate a-SiN_x:H/SiO₂ multilayer structures based light emitting devices. An effective and efficient method for electric current injection is proposed for the multilayer structure where the electric field is applied parallel to the multilayer structure. In this way, the current passes only through the well layers and does not encounter the energy barriers presented by the SiO₂ layers. We have also fabricated electroluminescent devices with conventional vertical injection in a direction that is normal to the multilayers, to serve as a comparison to the lateral devices.

1.3 Achievements

In this work efficient light emitting a-SiN_x:H thin films with uniform and controllable thicknesses have been successfully fabricated in single and multilayer structures using the PECVD technique. Detailed studies on the optical properties and light emitting characteristics of the fabricated samples, including the single layer films and multilayer structures have been performed. The samples were found to exhibit PL in visible range at room temperature, with emission characteristics that are tunable by varying the source gases SiH₄/NH₃ gas flow ratio. The optical properties of this group of material were studied in detail using spectroscopic ellipsometry. To ensure good accuracy and uniqueness in the fitting of the ellipsometry data, the data for each sample was acquired at five incident angles in a wide energy range (0.7 eV to 4.5 eV). To analyze the data, three competitive models, Tacc-Lorentz (TL), Tauc-Lorenz-Urbach (TLU) and Cody-Lorentz-Urbach (CLU) were used and their corresponding results were compared. The TLU model was found to be the most suitable in describing the dispersion relation of this group of a-SiN_x:H materials. The optical bandgap, refractive index and absorption coefficient of the materials were obtained from the fitted data and found to be well correlated to the PL characteristics.

This optimum condition that gave rise to efficient emission for a-SiN_x:H was used to grow the well layers in a-SiN_x:H/SiO₂ multilayers. Two samples with fixed SiO₂ barrier layers of 10 nm and a-SiN_x:H well layer thicknesses of 3 and 6 nm were successfully fabricated by controlling the deposition time. TEM micrographs of the samples verified the thicknesses, thickness uniformity and abrupt interfaces of the multilayers.

Despite the complicated multilayer structures that comprise 20 layers of very thin materials, we have successfully developed an optical model to fit their ellipsometry data and deduced

the optical properties of the a-SiN_x:H well and SiO₂ barrier layers. Tauc-Lorentz and Cauchy dispersion formula were used to describe a-SiN_x:H and SiO₂ materials respectively. The quality of the fit was evaluated by the mean square error and also by comparing the results with those obtained using TEM to validate their correctness. The complex refractive indices and optical bandgaps of the samples have been determined from the fitted dispersion models and found to be well correlated to the PL results.

We have demonstrated electroluminescent (EL) from a a-SiN_x:H/SiO₂ multilayer structure grown by the PECVD technique with a lateral current injection scheme. The multilayer is sandwiched between two heavily doped n and p poly-Si regions to form a PIN structure. Electric current is injected parallel to the multilayer structure and as a result flows mainly through only the well layers but not the barrier layers. Compared to a similar multilayer structure with a conventional vertical injection method, the current density is enhanced by more than nine orders of magnitude.

1.4 Organization of the Report

Chapter 1 presents motivation, background and objective of the research performed and a summary of the results obtained. In Chapter 2 an introduction to amorphous materials and quantum confinement will be presented, followed by a review of light emission from various Si based materials and nanostructures. Chapter 3 describes the experiments done to fabricate and characterize a series of a-SiN_x:H films and amorphous multilayer structures as well as the a-SiN_x:H multilayer electroluminescent devices. Chapter 4 presents a detailed comparison between the three different dispersion models (Tauc-Lorentz, Tauc-Lorentz-Urbach and Cody-Lorentz-Urbach) for a-SiN_x:H thin films. The PL and ellipsometry results of a series of single layer a-SiN_x:H films with different stoichiometries are discussed in Chapter five. The

detailed modeling procedure of ellipsometry data, including a comparison between the three different dispersion models (Tauc-Lorentz, Tauc-Lorenz-Urbach and Cody-Lorentz-Urbach) for this group of single layer a-SiN_x:H films will be reported. The effect of thermal annealing on the structural, optical and emission properties of such a-SiN_x:H films is also investigated in this chapter. The complex refractive indices, optical bandgaps, and Urbach energies deduced are discussed and correlated to the PL results. In Chapter 6, multilayer structures will be investigated. The detailed analysis of the ellipsometry data to obtain the optical properties of the individual well and barrier layers, including the optical model development and data fitting process, will be explained. The results obtained are discussed and correlated to the TEM pictures of the structures as well as their light emitting characteristics. In addition, the EL results of the multilayer structure utilizing lateral current injection will be presented in this chapter. Finally, Chapter 7 contains the conclusion and the future work of this project.

Chapter 2 LITERATURE REVIEW

2.1 Electronic Structure and Optical Properties of a-Si

Amorphous Si (a-Si) is the non-crystalline form of Si. The atomic structural disorder is the main characteristic that distinguishes amorphous from crystalline Si. Unlike crystalline materials which are characterized by the periodicity and symmetry of their lattice, amorphous ones are more described by the chemical bonding between atoms with emphasis on the short range bonding interactions rather than long range order [89]. Consequently, the abrupt band edges of the crystalline materials are replaced by a broadened tail of states extending into the forbidden gap, which originates from the structural disorder [90-92]. Bandtail states are important because electronic transport occurs at the band edges [37]. As depicted in Fig. 2.1. The electronic structure of an amorphous semiconductor comprises the valence and conduction bands, the corresponding band tails and the defects states in the gap. The latter is attributed to a departure from the ideal network (such as coordination defects) leading to electronic states deep within the bandgap [37, 89, 93].

Fig. 2.1 Schematic density of states distribution for an amorphous semiconductor showing the bands, the band tails and the defect states in the band gap. The dashed curves are the equivalent density of states in the crystalline counterpart [89]

One of the most important optical transitions in semiconductors is absorption. It happens when a photon is absorbed by an electron, resulting in its transition to a higher energy level. In the case of crystalline semiconductors, both energy and momentum must be conserved during an absorption process [94]. However, for amorphous semiconductors this conservation rule is relaxed due to the disorder [94]. That is the reason why the distinction between direct and indirect transitions is absent in a-Si:H and other amorphous semiconductors. The lack of momentum conservation in the amorphous phase also removes the sharp absorption features exhibited by crystalline semiconductors [89]. Optical absorption in a material is described by its absorption coefficient $\alpha(\lambda)$, which is a function of the imaginary part of its complex refractive index $N(\lambda)=n(\lambda)+i k(\lambda)$,

$$\alpha(\lambda) = 4\pi k(\lambda) / \lambda \quad (2.1)$$

where λ is the wavelength of light [89]. For amorphous semiconductors, a typical absorption coefficient versus photon energy plot is similar to that shown in Fig. 2.2. The regions B and C are created by transitions within the fully coordinated system perturbed to some extent by defects (fundamental absorption), while region A arises from transitions involving the defect states directly [94].

Fig. 2.2 Schematic representation of the absorption spectrum in amorphous semiconductors. The regions A, B and C are discussed in the text [94].

The optical bandgap of amorphous semiconductors can be determined using the Tauc equation:

$$(\alpha h\nu)^{1/2} = B^{1/2}(h\nu - E_g) \quad (2.2)$$

where α , $h\nu$ and E_g are the absorption coefficient, incident photon energy and Tauc optical bandgap respectively and B is a constant [94]. By extrapolating the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ curve, E_g can be determined as the energy axis intercept. Urbach energy (E_u) which is another important parameter to describe the optical properties of amorphous materials, is characterized by the exponential slope of region B in Fig. 2.2.

Photon emission is the reciprocal phenomenon of absorption. It happens when a previously excited electron falls to a lower energy state and releases its energy as a photon. The electron can be initially excited to higher energy by photons, electric current or a beam of high-energy electrons. The emission occurred after these types of excitations are called photoluminescence (PL), electroluminescence (EL) and cathodoluminescence respectively. The radiative recombination process in amorphous semiconductors typically comprises two sequential steps as illustrated in Fig. 2.3 [37, 38, 89, 93]. An excited electron or hole first loses energy by thermalization involving many transitions within the conduction or valence band respectively, in which the energy decrements are small but frequent. Eventually, the electron completes the recombination by making a transition to a hole with the release of a large energy as a photon [89]. If the charge carriers recombine without releasing photons the process is considered as nonradiative recombination, the primary effect of which is reduction in emission efficiency. Nonradiative recombinations may occur through carrier tunneling to defect states, diffusion through thermal ionization in which the electron is thermally re-excited to the

conduction band [93]. Another nonradiative mechanism in a-Si is Auger recombination in which the energy of the recombination event is transferred to another electron in the conduction band [93].

Fig. 2.3 Illustration of electron-hole recombination, showing thermalization and different recombination mechanisms [89].

2.2 Light Emission from Amorphous Silicon based Materials

Amorphous Si and its alloys with oxygen (O), nitrogen (N) and carbon (C) have been studied in the pursuit of Si based light emitting materials. Since amorphous semiconductors are not constrained by crystal momentum conservation, they can have high emission efficiencies [36-38, 89]. a-Si:H has a bandgap of only about 1.8eV, which limits its usefulness over the visible region of the electromagnetic spectrum. By adding alloy constituents such as N or C to a-Si:H, one can increase the energy gap, making it possible to have luminescence in the visible range, whose energy can be tuned by altering the composition of the material [21, 32, 33, 59].

Hydrogenated amorphous silicon carbide (a-SiC:H) thin films have been investigated because they are not only a promising material for fabricating efficient solar cells [95-98] but are also interesting and useful for the study of the characteristics of amorphous materials [40]. The physics of these alloys is more complex due to the presence of carbon that can exist in different bonding configurations. As the atomic ratio of C to Si can be varied from 0 to 1, the optical gap can be tailored over a wide range [21, 24-27, 46]. A detailed understanding of the plasma deposition conditions such as total gas flow, RF (radio frequency) power, substrate temperature, and electrode distance, which determine the composition of the plasma and consequently the atomic fractions of the different elements in the growing film, is essential for the optimization of the optoelectronic properties of the films [40, 47, 99, 100]. Many studies have been carried out to investigate the effect of these parameters on the film characteristics [21-27, 40, 45, 46, 48, 95, 99, 101-103]. There have been some reports that focused primarily on the optical properties and emission characteristics of a-SiC:H. For example, emission of blue light from a-SiC:H deposited using xylene as the source of carbon was reported by Nevin [24]. Effects of microwave power and radio frequency bias voltage on the structural and emission properties of a-SiC:H deposited by electron cyclotron resonance chemical vapor deposition (ECR-CVD) have also been studied [25, 26]. The PL behaviors observed are interpreted using bandtail states recombination model for amorphous semiconductors with wide tail widths. Films containing nanocrystalline 3C-SiC embedded in an amorphous SiC matrix have been fabricated by hot-filament CVD employing methane and silane as the

precursors [48]. The high resolution transmission electron microscopy images showed that these films contained embedded nanocrystallites with an average dimension of about 7 nm. X-ray photoelectron spectroscopy, X-ray diffraction, infrared absorption, and Raman scattering studies have revealed the presence of 3C-SiC nanocrystals. The films displayed strong visible emission at 2.2 eV that appeared to stem from the nanocrystalline 3C-SiC. Hydrogenated nanocrystalline silicon carbide films have also been produced using a similar method [23]. The films which contained SiC nanocrystals embedded in a-SiC:H matrix produced a strong emission peak at 2.64 eV. Time-resolved PL spectra have been acquired from SiC nanocrystalline films deposited on Si using the ECR-CVD technique [101]. Optical absorption measurements showed a clear blue-shift of the band gap with decreasing nanocluster sizes.

Another interesting amorphous material, a-SiN_x:H, has been extensively used in the past few decades in microelectronics industry for a wide variety of applications including oxidation mask, dopant diffusion barrier, gate dielectric in field effect transistors, encapsulation for III-V semiconductors, interlayer dielectric and final passivation layer for device packaging [104-108]. In recent years, hydrogenated a-SiN_x:H thin films have attracted great interest due to their potential applications in optoelectronic devices such as optical waveguides [109, 110] and antireflection coatings in solar cells [111].

In addition to the above mentioned applications, a-SiN_x:H is an attractive potential candidate for light emitting applications. Its optical band gap can increase monotonically with x from 1.9 to 5 eV [33], providing a wide energy range for tuning the emission wavelength. Deshpande et al. have studied various a-SiN_x:H samples deposited by the hot filament chemical vapor deposition (HFCVD) technique and reported optical bandgaps between 2.4 to 4.7 eV [31]. They observed three broad peaks at 1.8, 2.4 and 3.0 eV in the PL spectrum. As shown in Fig. 2.4, they have explained the observed PL with a qualitative model based on nitrogen and Si dangling bonds.

Fig. 2.4 Model for PL in a-SiN_x:H films [31]

Aydimli et al presented the results of PL and structural characterization of a-SiN_x:H deposited by plasma enhanced chemical vapor deposition (PECVD). Based on their Fourier Transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis, they proposed that the origin of visible PL in their samples is due to clusters of Si with different sizes in the films [59]. They suggested that the size of these clusters is smaller in the case of samples grown with a lower ratio of NH₃

to SiH_4 . The PL red shift and its intensity enhancement observed were assigned to an increase in the Si cluster size and the improvement in their crystallinity respectively [59]. In a similar study by Molinary et al., IR absorption and Raman scattering results indicated the presence of hydrogenated Si regions in a Si nitride matrix [34]. According to their conclusions, by increasing the N_2 flow ratio (which is the source of nitrogen in their experiments) in the films, the Tauc bandgap increases due to the greater nitrogen concentration in the $\text{a-SiN}_x\text{:H}$ matrix and more efficient passivation of the Si dangling bonds. The PL intensity also increased continuously and was explained by a greater number of Si clusters and a decrease in the density of defects through increasing the N content. Moreover, a PL blue shift was observed, attributed to the more extended Si-N region that surrounds more but smaller Si domains [34].

In a detailed study, Giorgis et al have investigated the emission characteristics including spectroscopic and time resolved PL of $\text{a-SiN}_x\text{:H}$ films as well as their optical absorption spectra to determine how absorption and emission are correlated [33]. They have observed that as the N content increases, two systematic trends were noted; that is, the PL spectra shifted toward higher energies and were broadened. Further analysis of the PL broadening and its correlation with the Urbach energy revealed that the observed PL broadening is linked to the existence of band tail states due to topological disorder, a consequence of N incorporation. The luminescence decay is also linked to the density of states shape, in particular

the spectral dependence of the lifetimes is a consequence of the widened tail states distribution [33].

2.3 Transport properties in a-Si based materials

In the previous sections we have reviewed mostly the structural, optical and light emitting properties of a-Si based materials. Since realization of electroluminescent devices is within the scope of this work, a review on the electronic transport properties of such materials is presented in this section. Amongst these properties the one that is important for investigating electroluminescent devices is the electrical conductivity [89, 112]:

$$\sigma(E) = N(E)e\mu(e)KT \quad (2.3)$$

where $N(E)$, e , $\mu(E)$ and KT are carrier density, the electron charge and the Boltzaman factor respectively. The dominant conduction path in semiconductors is determined by the carrier density and their mobility [89, 112]. In a-Si:H conduction takes place by electrons or holes at the band edges where both the density of states and the mobility increase with energy [89, 113]. For low electric fields multiple trapping in exponential bandtails has been remarkably successful for electron and hole drift mobility measurements in the entire class of amorphous silicon alloy materials [114-117]. For high field effects observed in electron drift mobility measurements a description of high-field generalizations of the bandtail multiple-trapping model have been proposed [116].

One of the conduction mechanisms to explain current transport in thin a-Si alloys is the Poole Frenkel (PF) emission mechanism [118, 119]. In this model the current density and the electric field are correlated with the following relation [118-122]:

$$J \propto E \cdot \exp\left(\frac{-q(\phi_B - \sqrt{\frac{qE}{\pi\epsilon}})}{k_B T}\right) \quad (2.4)$$

where J is the current density, E is the applied electric field, q is the elementary charge, ϕ_B is the voltage barrier that an electron must cross to move from one atom to another (in zero applied voltage condition) and ϵ is the dynamic permittivity [118-122].

It is shown that the PF effect is a limiting case of a more general analysis. At low temperature conduction is by tunneling emission out of the defects into the quasi-conduction band of the host material whereas at high temperatures thermal emission becomes dominant [122]. Electrical characterization of radio frequency sputtered a-SiC:H films in [123] shows that hopping and PF effects are the conduction mechanisms for low and high applied fields, respectively [123].

Similarly, PF mechanism has been repeatedly reported as the responsible conduction process in a-SiN_x:H films at low temperatures [118] and high [124] or low fields [125]. Another current transport mechanism commonly identified in such devices is the Fowler-Nordheim tunneling which predicts a linear relationship between $\ln(I/V^2)$ and V^{-1} [118, 126, 127]. Depending on the working temperature

or applied electric field level, a combination of both mechanisms has also been observed in a-SiN_x based materials and devices [118].

2.4 Light Emission from Silicon Nanostructures

The studies reviewed in the previous section concentrated mainly on the PL and its mechanism in the Si alloys and the behavior of the luminescence process as a function of the alloy concentration. Since the report of intense PL from electrochemically etched Si by Canham [60], interest in Si-based visible luminescence was renewed. Many attempts were made to investigate PL in materials containing structures of Si that are only a few nanometers in size in one or more spatial dimensions [50, 54, 64, 128]. The various types of nano-scale Si and their optical and luminescence properties reported so far will be summarized in this section.

2.4.1 Porous Si

Electrochemical etching of Si wafers, which results in porous Si (PS), is one method of obtaining nanoscale crystalline Si clusters. Porous Si has received much attention as a candidate for Si based optical devices since 1990 when Canham first observed visible PL from this structure [60]. Visible luminescence ranging from green to red was soon reported for other PS samples and ascribed to quantum size effects in the Si nanostructures formed in PS [61, 62, 128, 129]. The PL peak wavelength and intensity are sensitive to the surface chemistry of PS, particularly with regard to the relative amounts of hydrogen and oxygen on the surface. Thus,

besides the quantum confinement mechanism, various surface states and defects models have been invoked to explain the results obtained [130, 131]. Despite its efficient luminescence, the PS approach has a drawback arising from the high reactivity of the sponge like texture which causes rapid aging of the structure and an uncontrollable variation of the emission characteristics with time.

2.4.2 Si quantum dots in an insulating matrix

Creating nanocrystals of Si embedded in a dielectric matrix is another established way to obtain Si nanostructures. This approach has received wide spread acceptance especially after the report by Dal Negro et al. in Nature demonstrating optical gain in a Si-nanocrystal (Si-nc)/SiO₂ system [64]. They measured the optical gain using variable strip length method under intense laser oxidation. The fabrication challenges included achieving a high quality oxide, high density of nanocrystals and placing them in the core of the waveguide [64]. This work became the motivation for many subsequent attempts to achieve light emission from similar structures [19, 67, 68, 73, 132-142]. In addition to the possibility of having optical gain, these structures are favorable for device fabrication when compared with PS because of the increased surface stability and material rigidity [143]. Different approaches such as sputtering [144] and ion implantation [145] have been used to achieve nanoclusters of Si in a dielectric matrix. Besides, plasma vapor deposition of Si alloy thin films that contain excess Si is another widely used method to achieve Si nanoclusters [34, 54, 59, 146]. The luminescence properties of Si nanoclusters in these films are very similar to those of PS, with a wide

emission band observed at room temperature and spectral position that depends on the Si nanocrystal sizes [132, 134, 142, 147]. The size of the crystallites in these films can be controlled by the amount of excess Si and thermal annealing that promotes the aggregation of excess Si atoms and results in their crystallization [70, 148, 149]. From the strong dependencies of the PL spectra on the Si nanocrystal size, it is concluded that the origin of the PL peak is attributed to radiative recombination of carriers inside the Si nanocrystals, whose energy gaps can be controlled through their size as a result of the quantum size effects [70, 132, 148-150]. However, for nc-Si/SiO₂ matrix structures, the tuning of the emission colors, particularly in the short wavelength region continues to be a challenge because the Si/dielectric interface is also thought to have played an important role in the optical properties and formation of the radiative states [130, 139, 151, 152].

For optoelectronic device applications, Si quantum dots in a Si nitride matrix is advantageous over a Si oxide matrix because electrons and holes can be easily transported to the a-Si quantum dots (QD) due to its lower tunneling barrier [52, 54, 146, 147, 149, 150, 152-159]. Aydmli et al. [59] studied Si clusters in Si nitride and for near stoichiometry Si nitride, they observed PL with a peak energy of 2.5 eV, which was attributed to quantum confinement of electron hole pairs in the Si clusters. Park et al. have demonstrated the growth of a-Si QDs in a silicon nitride film by plasma enhanced chemical vapor deposition using N₂ as the nitrogen source [54]. PL and optical absorption energy measurement of the a-Si QDs with various sizes revealed that tuning of the PL emission from 2.0 to 2.76 eV is

possible by controlling the size of the a-Si QDs. This size dependence observed was also explained by the quantum confinement effect. Kim et al. [160] have used NH_3 as the source of nitrogen to enhance the PL efficiency of a-SiN_x:H materials. They have attributed this enhancement to the hydrogen passivation of dangling bonds, which act as nonradiative centers. Using TEM and Raman measurements, Hao et al have shown that the red light emission observed in their a-SiN:H samples was originated from Si quantum dots [161]. They also observed a green and a blue band in their PL spectra that they have attributed to bandtail radiative recombination and recombination Si dangling bonds respectively [161]. Positive optical gain has been demonstrated recently by Monroy et al. in such structures [162]. Although the confined cluster sizes can be controlled to some extent by adjusting the amount of Si in the films and/or annealing temperature, achieving a uniform cluster size in the dielectric matrix and overcoming the effect of surface states in light emission mechanism remain a challenge [157, 163].

2.4.3 SiGe Nanostructures

It would be a common assumption that SiGe crystalline alloys could not exhibit photoluminescence since both c-Si and c-Ge are both indirect bandgap materials. However, low temperature light emission has been observed in bulk SiGe due to strong compositional disorder, which partially relaxes the carrier recombination selection rules in such materials. This type of luminescence in SiGe bulk alloys has little practical importance since the luminescence intensity is quickly quenched as the temperature increases [164-167]. Alternatively, Si/Si_{1-x}Ge_x multilayers were

intensively studied as a possible method to confine electron-hole pairs in quantum-well (QW) configurations and to reduce the luminescence thermal quenching [168-170]. High-quality Si/Si_{1-x}Ge_x QWs with low density of dislocations can be grown using only a relatively narrow processing growth window [171, 172]. Moreover, the PL quantum efficiency thermal quenching remains the unresolved problem for practical light emitters [164, 173]. A different form of SiGe nanostructure is three-dimensional (3D) self-assembled system. Compared to two-dimensional (2D) Si/SiGe multilayers, higher PL and EL quantum efficiency has been found in 3-D Si/SiGe nanostructures [164, 174-177]. The challenges associated with Si/SiGe nanostructure are luminescence efficiency, speed, and more critically their potential compatibility with the standard CMOS process [164, 178, 179].

2.4.4 Nanometer multilayer structures

Another approach in utilizing Si nanostructures for optoelectronic devices is based on multilayer structures [77, 82, 180-182]. Similar to other Si based nanostructures discussed above, quantum confinement effect and its advantages such as enhancement of PL efficiency and tunable emission wavelength are applicable to the multilayer structures as well. Besides, amorphous multilayer structures are more compatible with CMOS fabrication technology compared to porous Si. In addition, it is possible to precisely control the thicknesses of the layers by adjusting the deposition parameters. This renders them advantageous as their emission wavelength can be well controlled. Amorphous Si based multilayers are also attractive when utilized in EL devices because an efficient electrical pumping

scheme can be achieved by tunneling of carriers through the very thin barrier layers [77, 79, 183]. These advantages have rendered a-Si based multilayer structures very promising towards realizing Si based light emitting devices.

Abeles and Tiedje have reported the synthesis of this class of superlattice materials consisting of alternating layers of semiconductors, such as a-Si:H, a-SiN:H, a-Ge:H and a-SiC:H, and barrier layers deposited using the PECVD technique [184]. The stringent requirements for lattice matching in crystalline superlattices are relaxed in the amorphous case because of non-periodic structure and the ability of hydrogen to passivate coordination defects [184]. To determine the role of quantum size effect on the electronic structure of the amorphous semiconductors multilayer structures, optical absorption and PL of a-Si:H/a-SiN_x:H samples with a range of a-Si:H layer thicknesses were measured [184]. The absorption coefficient was found to decrease for thinner a-Si:H layer and correspondingly the Tauc optical bandgap showed a gradual increase, which is consistent with the quantum confinement effect [184].

In a similar study Kalem has investigated the optical properties of a-Si:H/a-SiN_x:H superlattices [185]. A blue shift in the bandgap was observed when the confined well layer thickness was decreased, which constituted the main evidence of quantum confinement effect. The changes seen in the optical bandgap were suggested to be due to the quantization of the extended states in the a-Si well layer

since they are in good agreement with a one dimensional quantum well model [185]. The Urbach energy also showed a trend with the well layer thickness which was attributed to an increased structural disorder in the material with decreasing well layer thickness. Using optical transmission and luminescence excitation measurements, Murayama et al. determined the fundamental absorption edge spectra of thin a-Si:H/a-Si₃N₄:H multilayers [186]. In their study, they have obtained similar results as reported by Kalem and Abeles et al. [184, 185] in the high-energy range of the absorption coefficient. However, the absorption in the low absorption region was found to be almost equal to that of bulk Si. Thus, it was concluded that the extended states in a-Si:H exhibit an energy shift due to quantum confinement effect, while the localized bandtail states exhibit no significant energy shift [186].

Giorgis et al analyzed the optical and radiative characteristics of structures composed of wide-bandgap a-SiN_x:H nanometric multilayers [80]. They have observed an enhancement in the PL efficiency in the well layers by decreasing their thickness and assigned it to the localization of electron hole pairs, which is stronger in thinner layers. They have explained the blue shift in the PL with decreasing well layer thickness by the quantum confinement effect within the effective mass theory. They have also measured the emission decay times in multilayers, which were noted to be larger compared to single-layer alloys and have weaker energy dependence. These results were explained by taking into account a widening of tail states in the well layer due to static disorder and a decrease of band edge states[80].

The results obtained by Rizzoli et al also indicated similar conclusions and ruled out the interface alloying model as the origin of the PL blue shift [187].

Another class of amorphous Si based multilayer structures of a-Si/SiO₂ has been studied by Lu et al. [81, 180]. They observed a red shift in the PL peak energy as the a-Si layer thickness was increased, indicating that the PL originates from the a-Si layers, in agreement with the quantum confinement model. However other studies of EL from Si/SiO₂ superlattices showed that the EL peak was hardly shifted with the Si layer thickness [183]. Different luminescence mechanisms have been proposed for the Si/SiO₂ superlattices. One is emission via the interface states [188] and another is the recombination of electron hole pairs through the band tail states in the a-Si layers [181, 189]. Averbokh et al. reported their measurements of both PL and EL from Si/SiO₂ multilayers fabricated by sputtering [190]. For EL experiments, a semitransparent gold film was deposited onto the cap layer as the negative electrode, while an aluminum layer deposited on the back of substrate was used as the positive electrode. Based on the insensitivity of the luminescence spectrum and PL decay lifetime on temperature and excitation wavelength, they suggested that the emission originated from transitions between localized defect states residing at the Si/SiO₂ interface [190]. Contribution of surface defect states in the light emission from Si/SiO₂ multilayers counteracts the wavelength tunability that is controllable through the nanostructures sizes [131]. In contrast, a-Si and a-Si₃N₄ interface do not suffer from surface states problem and therefore a-Si/Si₃N₄ multilayers are suggested to be better candidates for microphotonic

applications [76-78, 80, 86]. In a comparative study, Baribeau et al. [191] demonstrated the growth and characterization of a-Si/SiO₂ and a-Si/a-SiN_x multilayers with an in situ method using the ECR-PECVD technique. According to their depth profiling of a-Si caps on thin insulating layers, substantial oxygen contamination was detected in the a-Si well layers. Their a-Si/SiN_x multilayers, on the other hand, revealed no contamination [191]. Another important advantage of utilizing Si nitride as the barrier layer for a-Si based multilayers is the lower electron/hole injection barrier between a-Si/a-Si₃N₄, compared to a-Si/SiO₂ [77-79] which is particularly important for EL applications. In 2007 Tan et al. demonstrated PL and EL from a-Si/Si₃N₄ multilayer structures with a-Si well layer thicknesses of 3, 5 and 7 nm, while keeping the Si₃N₄ barrier thickness fixed at 10 nm [76, 77, 86]. The PL exhibited a thickness dependent peak energy that was explained by quantum confinement effect. Their Raman and selected area electron diffraction verified the amorphous state of their well layer even after annealing at 700° C. To fabricate the EL device a vertical injection structure was used with heavily doped poly silicon deposited on the top and bottom of the multilayer structure serving as positive and negative electrodes respectively. Subsequently other groups have reported EL obtained using similar structures as well [79, 192].

As presented above in the review of multilayer structures, many works have attempted to control the emission wavelength by adjusting the well layer thickness [76, 77, 80-82, 86, 180, 185]. Rui Huang et al on the other have demonstrated the tuning of the emission wavelength of a-Si/SiN_x structures by controlling the barrier layer stoichiometry [78]. It was found that a higher concentration of N in barrier

layer will lead to a lower peak energy wavelength. This phenomenon can be explained by the stronger confinement provided by the N rich barrier layers having a larger bandgap [78].

2.5 Spectroscopic Ellipsometry Study of a-Si based Materials

In this work we have extensively used spectroscopic ellipsometry to characterize the optical properties of single and multilayer samples. Ellipsometry measures changes in light polarization upon reflection from the samples and can be used to determine the film thickness and optical constants [193-196]. To obtain such information from the raw ellipsometry data, it is necessary to develop an optical model, select appropriate dispersion relations for the thin films and perform a fitting process. In this section, we review the ellipsometry techniques used for the characterization of optical properties of a-Si based materials. Various dispersion relations reported in the literature to model a-Si based materials will also be surveyed and discussed.

Accurate determination of optical properties of a-SiN_x:H thin films, including optical band gap, Urbach energy, and wavelength-dependent complex refractive index, is crucial for their designs and applications in optoelectronic devices. As stated previously, these optical properties of amorphous materials are highly dependent on their deposition conditions such as RF power, gas flow ratio, deposition temperature and chamber pressure etc [21, 25-27, 32, 33, 59, 197-199].

Therefore it is necessary to be able to accurately determine these quantities in the optical characterization of a-SiN_x:H thin films. Many techniques have been used and the most common of which is transmission-reflection (TR) spectroscopy. In this technique, the sample is radiated by a monochromatic beam of light. The intensity difference of a reference beam and the transmitted/reflected beam from the sample is measured and used for determination of its absorption coefficient at different wavelengths. The Tauc bandgap is then calculated using the Tauc formula shown in eq. (2.1). The optical bandgap of a-SiN_x:H was determined with this method by Austin [200] et al and Kurata et al [201]. Z.Yin et al [202] have determined the complex dielectric function of a-SiN materials by modeling the TR data using the Bruggemann effective-medium approximation.

This TR method, though simple in terms of measurement and data analysis, is incapable of determining accurately the absorption coefficient in the low-energy part of the spectrum. This is attributed to the small difference between the reference and transmitted beam intensities as a result of very weak absorption of the materials [203]. As the tail state transitions in amorphous materials determine their optical and emission characteristics to a very large extent [32, 37, 89, 91, 204, 205], it is necessary to have an optical characterization technique that can cater for the low-energy part of the spectrum. Giorgis et. al. have addressed this issue by measuring the low energy absorption of a-SiN_x:H materials using photothermal deflection spectroscopy (PDS) method and extrapolating the data with those obtained by TR spectroscopy [32]. They have subsequently used their absorption

data to calculate the Tauc bandgap as well as the Urbach energy of a-SiN_x:H and correlated them to the PL characteristics. Though accurate, the PDS technique is experimentally very involved and requires very extensive and elaborate equipment set up [206, 207]. Moreover, it does not provide absolute values of absorption coefficient and a matching of the data to the high energy spectrum measured by other techniques is necessary.

Compared to the TR and PDS techniques, the spectroscopic ellipsometry is a simpler and yet more sensitive and accurate technique for the optical characterization of a-SiN_x:H films. The challenge is to be able to identify a dispersion model suitable for a-SiN_x:H that can fit the ellipsometric data well, and from which their optical properties can be determined. Several such dispersion models exist that have been used to model the optical properties of amorphous semiconductors [194]. Forouhi-Bloomer dispersion model has been successfully used to describe the optical properties of several amorphous materials [208], including amorphous carbon films [209, 210]. However, there are several fundamental problems associated with this model. In the Forouhi-Bloomer model, $k(E) = 0$ at $E = E_g$ and $k(E) > 0$ for $E < E_g$. This is not physical as clearly inter-band transitions cannot result in optical absorption for $E < E_g$ when $k(E) = 0$ at $E = E_g$. It is not Kramers-Kronig (KK) consistent [211]. KK consistency implies that the complex refractive index has to be analytical in the upper half-plane, which is always the case for physical response functions due to causality. All the above problems were addressed with the introduction of Tauc-Lorentz model by Jellison

and Modine [212]. This new parameterization is obtained from the Tauc joint density of states and the standard Lorentz calculation for ε_2 of a collection of non-interacting atoms. If only a single transition is considered, $\varepsilon_2(E)$ is given by:

$$\varepsilon_2(E) = \begin{cases} \frac{1}{E} \frac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2 + C^2E^2}, & \text{for } E > E_g \\ 0, & \text{for } E < E_g \end{cases} \quad (2.3)$$

Where A , E_0 , C and E_g are the amplitude, the peak transition energy, broadening parameter and the optical band gap respectively. The real part ε_1 of the dielectric function is obtained using analytical integration of the Kramers-Kronig relation for $\varepsilon_2(E)$ [212]:

$$\varepsilon_1(E) = \varepsilon_{1,\infty} + \frac{2}{\pi} (C.P.) \int_0^\infty \frac{\zeta \varepsilon_2(\zeta)}{\zeta^2 - E^2} d\zeta \quad (2.4)$$

It is important to note that the Tauc optical bandgap is a model parameter and is obtained directly when ellipsometry data has been successfully fitted, rather than based on non-parameterized methods that require curve fitting. Since then, Tauc-Lorentz (TL) parameterization has been widely used and become the standard dispersion model for amorphous semiconductors and amorphous materials [88, 197, 212-217]. Vamvakas et al. used the TL model to fit the SE data of their low pressure chemical vapor deposited a-SiN_x:H containing Sinanocrystals [216]. An investigation of the annealing effect on the refractive index of their samples was performed. The work by Leliviere et al focused on the optical and PL properties of a-SiN_x:H deposited with different stoichiometry [197]. Complex refractive indices

of the films were determined by fitting the SE data in the energy range of 1.5 eV to 5 eV using the TL model. The absorption within the a-SiN_x:H layer was correlated to the PL characteristic. They reported a systematic trend of increasing PL peak wavelength with increasing n and k values, in agreement with previous studies that used other techniques [32, 59]. Cen et al applied the TL model and analyzed the evolution of the TL parameters to investigate structural changes in implanted Si embedded in a Si₃N₄ matrix [214].

Despite its success, the TL model does not include the Urbach tail, which is an important characteristic of amorphous semiconductors that accounts for defect induced absorption. Such band tail absorption decreases exponentially from the absorption edge and is particularly important for amorphous semiconductors since the band tail electronic states are known to play a crucial role in their optical absorption and emission behavior [33, 37, 89, 91, 204, 205]. This has prompted Ferlauto et al. to develop a new KK consistent model, known as the Cody-Lorentz-Urbach model, where three energy regions are assumed for the optical function: the sub-bandgap (Urbach region), the band to band onset region and finally the above bandgap region where a Lorentz oscillator model is assumed [218]. Two simple modifications of the TL expression are applied here: the inclusion of Urbach tail and the consideration of an additional transition energy as a fitting parameter. The imaginary part of the dielectric function is defined as [218]

$$\epsilon_2(E) = \begin{cases} \frac{E_1}{E} \exp\left\{\frac{(E - E_t)}{E_u}\right\}; & \text{for } 0 < E \leq E_t \\ G(E) L(E) = \frac{(E - E_g)^2}{[(E - E_g)^2 + E_p^2]} \\ \times \frac{AE_0 CE}{(E^2 - E_0^2)^2 + C^2 E^2}; & \text{for } E > E_t \end{cases} \quad (2.5)$$

Where $E_t \geq E_g$ is the demarcation energy between the Urbach tail of slope E_u and the band-to-band transitions of optical gap E_g . In eq. (2.5) the expression for $E > E_t$ includes the product of a Lorentz oscillator function $L(E)$ with amplitude A , resonance energy E_0 , and width C , and a band edge function $G(E)$. $G(E)$ forces $\epsilon_2(E)$ to assume a desired form for energies just above E_g . In addition, $G(E) \rightarrow 1$ for $E \gg E_g$ so that the desired result $\epsilon_2(E) \rightarrow L(E)$ holds at high energies. In Eq. (2.5), E_t is defined so that $\epsilon_2(E)$ is continuous at $E = E_t$; thus $E_t = E_t L(E_t) G(E_t)$. Eq. (2.5) generalizes the TL approach in that the Urbach tail is added and the function $G(E)$ is defined based on the assumptions of parabolic bands and a constant momentum matrix element with an additional parameter E_p . Here $E_g + E_p$ defines a second transition energy (in addition to E_t) that separates the absorption onset behavior from the Lorentz oscillator behavior. This second transition energy may provide more flexibility than the TL expression. The real part $\epsilon_1(E)$ is determined as usual from the KK transformation of $\epsilon_2(E)$ (eq. 2.3). Although this model was first introduced for a-SiC:H, it has been mostly used for the optical characterization of different materials such as As_4Se_3 [219], HfO_2 [220], $\text{Hf}_x\text{Si}_y\text{O}_z$ [221] and InN [215]. Although Cody-Lorentz-Urbach model has introduced some modifications and flexibilities to Tauc-Lorentz, it suffers from the disadvantage that three additional

unknown parameters have been introduced, which though may improve the fitting results, but can also lead to non-uniqueness in the model parameters obtained.

Another model that also considers the low energy Urbach absorption is the Tauc-Lorentz-Urbach (TLU) model [222]. Compared with the Cody-Lorentz-Urbach model, this model has the advantage as it offers continuity in the first derivative of the dielectric function. The imaginary part of dielectric constant in this model is defined as [222]:

$$\varepsilon_2(E) = \begin{cases} \frac{1}{E} \frac{AE_0 C (E - E_g)^2}{(E^2 - E_0^2)^2 + C^2 E^2}, & \text{for } E > E_c \\ \frac{A_u}{E} \exp\left(-\frac{E}{E_u}\right), & \text{for } 0 < E < E_c \end{cases} \quad (2.6)$$

where the first term ($E > E_c$) is identical to the TL function and the second term ($0 < E < E_c$) represents the exponential Urbach tail. The additional parameter E_c denotes the demarcation energy between the Urbach tail transitions and the band-to-band transitions. In Eq. (2.6) E_u is not a fitting parameter and is calculated based on the continuity of the optical function including first its derivative. Similar to the TL model, ε_1 is calculated using the KK integration. This model has been used to model the transmission and reflection data of a set of a-SiN [223]. Comparing the obtained results with the ones obtained by TL, an improvement was observed in the fitting quality which is attributed to addition of Urbach tail to the model [223].

To date all the three dispersion models (Tauc-Lorentz, Tauc-Lorentz-Urbach and Cody-Lorentz-Urbach) reviewed above have been used to describe the optical properties of amorphous materials by different research groups [88, 197, 211, 213-218, 220-222]. However, so far there is no detailed study performed to compare and contrast these models in terms of their accuracy when applied to a-SiN_x:H. As we will be using spectroscopic ellipsometry to study the optical properties of a-SiN_x:H in multilayer structures that involve many layers of well (a-SiN_x:H) and barrier (SiO₂) layers, it is important that we identify a model that is best suited for a-SiN_x:H in order to accurately determine their optical properties. In Chapter 4 a detailed analysis and comparison between these models when applied to our a-SiN_x:H will be carried out.

2.6 Conclusion

In conclusion, the previous published work to achieve light emission from Si based materials using different structures has been reviewed. The possible origins of PL from amorphous Si bulk materials and nanostructures have been presented. Amorphous Si based multilayer structures, fabricated using processes that are compatible with the VLSI technology, are noted to be potential candidates to realize efficient light emitters. In addition, different dispersion models that have been used for describing the optical properties of amorphous Si based materials are reviewed and compared.

Chapter 3 **EXPERIMENTS**

The experimental techniques used in this project will be described in detail in this chapter. Firstly, the plasma enhanced chemical vapor deposition (PECVD) technique that has been used for the growth of the films will be explained. This is then followed by the description of the single and multilayer samples deposition conditions. Various characterization techniques employed for the study of the films and analysis of the devices will be presented as well. These include transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), photoluminescence (PL), electroluminescence (EL) and current-voltage (I-V). Spectroscopic ellipsometry (SE) experiments including its working principles, instrumentation, data analysis and measurement details will be presented separately in Chapter 4, before reporting the corresponding results.

3.1 Film deposition

All the samples in this study were deposited on 8 inch p-type <100> Si substrates with a doping concentration of 10^{15} cm^{-3} , using an Applied Material Centura 5200 PECVD tool. PECVD is one of the most common approaches for deposition of thin films both in CMOS production lines as well as research laboratories [224-229]. Compared with the conventional CVD methods such as low pressure chemical vapor deposition (LPCVD), PECVD technique has the advantages of low process temperature, flexible film properties and high deposition rate [226, 229]. LPCVD process on the other hand produces layers with excellent uniformity of thickness

and material characteristics [230, 231].

Sputter deposition, commonly called sputtering is another standard technique used for the deposition of metals and dielectrics [227, 232]. In this technique atoms or molecules are removed from a solid target's surface and then projected into the gas phase from which they condense on another surface [227, 232]. The quality of the films grown by sputtering, which is a physical vapor deposition method, might be inferior to CVD, which for metals means higher resistivity and for insulators more defects and traps [233]. The step coverage is also not as good as CVD [224].

Another well-established technique for producing a wide variety of thin films is pulsed laser deposition (PLD) [225, 234]. In this technique the interaction of intense laser pulses with a target surface generates particles which show non-equilibrium characteristics during deposition; these excited species with high kinetic energies can lead to the formation and growth of films on the substrate [225, 234]. Main advantages of PLD technique are precise stoichiometry control and relatively high deposition condition [225]. On the other hand, small area deposition, generation of particulates [235, 236] and target surface modification [236] (affecting thin film uniformity) are drawbacks of this technique [225].

As mentioned previously, one of PECVD's advantages over thermally driven chemical vapor deposition (CVD) is its low temperature capability. An effective substitution of electrical energy (plasma) for thermal energy in the CVD

environment has made the low temperature capability possible. Low thermal budget processes are advantageous as they allow the use of lower cost and large area substrates such as glass [229]. The schematic of a typical PECVD system is shown in Fig. 3.1.

Fig. 3.1 Schematic diagram of a conventional PECVD system

We begin the PECVD technique description with some physics and chemistry fundamentals involved in a plasma. The glow discharge or plasma is defined as a partially ionized gas containing positive and negative charged species and is generated by applying a radio frequency (RF) electric field to the deposition chamber. The electric field accelerates charged particles present in the gas. Once these electrons acquire sufficiently high energies, their collisions with gas species result in excitations and ionizations, generating additional electrons accelerated by the electric field [226, 229]. This transient process avalanches quickly, creating the steady state plasma. The inelastic collisions between high-energy electrons and gas

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species give rise to highly reactive species such as free radicals and ions [226, 229]. Such reactive species have lower energy barriers to physical and chemical reactions than the parent species and consequently can react at lower temperatures. After creation of reactant species containing the elements to be deposited, they are transported to the vicinity of the wafer where they diffuse to the surface, adsorb on the surface, undergo chemical reactions and surface migrations, and eventually yield a solid film [226, 229]. Reaction byproducts are formed, adsorbed, diffuse away into the main gas stream, and are finally transported out of the chamber. A simplified summary of this sequence of steps is shown in Fig. 3.2 [226].

Fig. 3.2 The basic elements of the PECVD process: gas molecule dissociation by collision of high-energy electrons, transport of the activated species to the wafer surface and bonding to the film surface [226].

For the deposition of bulk single layer a-SiN_x:H films in this project, SiH₄, N₂ and/or NH₃ gases, which are conventionally used for deposition of such materials

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[50, 201, 202, 237-239], have been used as precursors. For the PECVD growth of SiO_2 films, N_2O and SiH_4 are commonly used as the O and Si sources respectively [240, 241] and are used in this project as well. The conditions used for the deposition of a- $\text{SiN}_x\text{:H}$ and SiO_2 are summarized in Table 3.1. 8 inch p-type c-Si wafer were used as substrates.

Material	Substrate Temperature ($^{\circ}\text{C}$)	Chamber Pressure (Torr)	RF Power (Watts)
a- $\text{SiN}_x\text{:H}$	400	5	350
SiO_2	400	3	270

Table 3.1 PECVD conditions for the growth of a- $\text{SiN}_x\text{:H}$ well and SiO_2 barrier layers in multilayer structures

Single layer a- $\text{SiN}_x\text{:H}$ films with different stoichiometries have been grown by changing the SiH_4 flow rate from 20 sccm to 120 sccm while keeping the NH_3 , N_2 and He flow rates constant at 38, 3300 and 1250 sccm respectively. Table 3.2 shows the samples' labels and the corresponding gas flow ratios $R = \text{SiH}_4/\text{NH}_3$.

Sample Label	SiH_4 (sccm)	$R = \text{SiH}_4/\text{NH}_3$
S12	120	3.16
S9	90	2.37
S6	60	1.58
S4	40	1.05

Table 3.2 Gas flow ratios of fabricated a- $\text{SiN}_x\text{:H}$ single layer films

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To grow the a-SiN_x:H/SiO₂ multilayers, the barrier layer SiO₂ thickness was fixed at 10 nm and different a-SiN_x:H well layer thicknesses of 3 and 6 nm were deposited as shown in Table 3.3. The samples each has a period of 10 well and barrier layers. Fig. 3.3 shows the detailed schematic of the multilayer structures fabricated, which consists of the multilayer sandwiched between a top and bottom layer of 50 nm SiO₂. The well layer deposition conditions were chosen to be the same as the sample S6 with $R=1.58$ and the thicknesses were precisely controlled by adjusting the deposition time. According to our studies which will be presented later in Chapter 5, at $R=1.58$ the grown films are more efficient in terms of light emission. To avoid intermixing of the layers, the RF power was stopped after each layer deposition and the chamber was evacuated before depositing the subsequent layer.

Sample Label	Number of Periods	a-SiN _x :H Well Layer Thickness (nm)	SiO ₂ Barrier Layer Thickness (nm)
M3	10	3	10
M6	10	6	10

Table 3.3 The structural information of the multilayer samples M3 and M6

Fig. 3.3 Schematic of multilayer structures fabricated in this study showing the number of layers and the thicknesses

For the study of a-SiN_x:H multilayer electroluminescent devices in this study, two different device structures have been fabricated. First is the conventional vertical injection device, where the electric current flows perpendicular to the plane of the multilayers. In this structure, which is commonly used for fabricating single/multilayer EL devices, the electrodes are designed to be on the top and bottom of the luminescent structure so that the electric field is applied in the vertical direction. Here, heavily doped Si substrate and poly-Si are used as the bottom and top electrodes respectively. The second structure fabricated in this work is a lateral injection device where the current flows parallel to the plane of

multilayer. The electrodes are designed to be on the two sides of luminescent multilayer. The process steps involved in the fabrication of the two device structures will be described in Chapter 6 before presenting their result and discussions.

3.2 TEM

Transmission electron microscope (TEM) is an advanced tool to characterize the microstructure of materials with very high spatial resolution [242]. In TEM high-energy electrons are accelerated at several hundred kV and focused with electromagnetic lenses on a very thin specimen. The image at atomic resolution is then observed on a fluorescent screen, or recorded on film or digital camera. Information about the morphology, crystal structure and defects, crystal phases and composition, and magnetic microstructure can be obtained by a combination of electron-optical imaging [243, 244].

In order to investigate the microstructure of the single layer films and to monitor the possible nucleation of Si nanocrystals or amorphous nanoclusters in Si-rich samples, we performed High Resolution Transmission Electron Microscopy (HRTEM) studies. As for the multilayers samples and electroluminescent devices, TEM experiments were used to determine the layer thicknesses, their uniformity and the quality and abruptness of the layers. TEM experiments were carried out using an FEI CM 200 tool at the A*Star Institute of Microelectronics, Singapore.

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To prepare very thin samples for TEM characterization, an FEI Nova 200 focused ion beam (FIB) tool was used, where a focused Ga^+ beam milled the samples to very small thicknesses less than 100 nm. Prior to performing FIB milling, the specimens surface were coated with a SiO_2 layer of about 1 μm thick in order to protect the surface during the ion milling. Machining begins with an ion beam of 20-30 keV under normal incidence. Starting from the external faces of the selected area of interest on the sample, two trenches are dug, one on each side, digging closer until a nanometer thick slice remains at the desired location. Next, the specimen is tilted by $0.5\text{-}1^\circ$ and the final thinning is performed at low ion beam energy (1.5-5 keV). The produced thin lamella slice is finally collected and used for the TEM imaging.

3.3 FTIR

Fourier transform infrared (FTIR) spectroscopy is one of the most widely used characterization techniques to study bonding configurations in thin films [245]. This method is fast, non-destructive and provides a high signal to noise ratio (non-dispersive spectrometry). In this technique, the molecules are radiated with an infrared source. When there is a change in the dipole moments during the vibration of the molecules, the mode of vibration is called infrared active. An infrared spectrum represents a fingerprint of a sample, with the absorption peaks correspond to the frequencies of vibrations between the atomic bonds. Therefore, it is possible to qualitatively determine the chemical bonds present in the material. In this study, FTIR measurements were performed on single and multilayer samples

using a BioRad system. The measurement resolution was set at 4 cm^{-1} and each spectrum was taken as an average over 32 scans from 400 cm^{-1} to 4000 cm^{-1} . The substrates were measured separately and served as the background. The system software corrected for the background automatically and determined the infrared absorption in the films.

3.4 Photoluminescence

Luminescence in general is the phenomenon in which electronic states of solids are excited to a higher energy level (by absorbing some forms of energy from an external source) and then return to a lower energy state accompanied by emission of a photon. The excitation energy can be in the form of short-wavelength light, electric field or cathode rays, which correspond to photoluminescence (PL), electroluminescence (EL) and cathodoluminescence phenomena respectively [246, 247]. Luminescence spectroscopy is performed by recording the emission spectrum as a function of wavelength. PL spectroscopy, which is a primary tool to develop light emitting semiconductors, is performed by illuminating the sample with an optical source of energy ($h\nu$) larger than the material's bandgap. This will generate electron hole pairs in the sample some of which will recombine radiatively and emit photons. The photon energy depends on the recombination process as shown in Fig. 3.4 (a) to (e): band to band recombination (a), free excitonic recombination (b), free hole with a neutral donor (c) free electron with a neutral acceptor and lastly (d) a neutral donor with a neutral acceptor (e) [248].

Fig. 3.4 Radiative transitions observed in PL [248]

By focusing the photons emitted from the sample onto a dispersive spectrometer, collecting them on a detector and finally recording them by a computer the PL spectrum is generated. PL spectroscopy is a versatile tool to unravel the sometime complicated energy levels within the bandgap of semiconductors and the electronic structure of localized centers [246, 247].

When the intensity and efficiency of luminescence are of interest, the PL internal quantum efficiency defined as follows can be studied,

$$\eta_{\text{int}} = \frac{\text{the number of photons emitted}}{\text{the number of photons absorbed}} \quad (3.1)$$

$$= \int_0^d \frac{\Delta n}{\tau_{\text{rad}}} \exp(-\alpha x) dx \approx \int_0^d \frac{\Delta n}{\tau_{\text{rad}}} dx$$

wher ed is the sample thickness, Δn the excess minority carrier density, and α the absorption coefficient of the semiconductor at the emitted wavelength. Δn depends

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on the reflectance, photon flux density and various recombination mechanisms in the sample.

A typical PL set up consists of an excitation source, an excitation monochromator (not when a laser is used as the light source), a sample compartment, an emission monochromator and a detector as outlined in Fig. 3.5. The PL spectroscopy instrumentations, optics and configurations are designed to ensure maximum light collection.

Fig. 3.5 The schematic of a typical PL system [249]

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Two categories of light sources, lamps and lasers can be used for PL measurements depending on the type of experiment, the required excitation power and wavelength and the cost and availability of tools. Lasers are advantageous as they have high power, small divergence, coherence, monochromatism and the capability of very short pulses [246].

The equipment used for the steady-state PL measurements in this study is a F900 fluorescence spectrometer which is shown in Fig. 3.6. Laser diodes with 371 nm and 266 nm emission wavelength and respective average powers of 0.1 mW and 10 mW were used as excitation sources in our PL studies. A Hamamatsu multi channel plate photo multiplier tube was used as the detector. The spectra measured were corrected for the optical response of the system.

Fig. 3.6 The F900 PL system used in this work. The major parts include the excitation source, sample compartment, emission monochromator and detector are shown

3.5 Electroluminescence

Electroluminescence (EL) is the phenomenon of light emission from semiconductors as a result of radiative recombination of electrons and holes, after being excited by an electric field. EL occurs basically in two forms, known as injection EL and high-field EL. In injection EL, light is emitted upon recombination of minority and majority carriers across the bandgap of a semiconductor or via localized/defect states within the bandgap. High-field EL consists of excitation of luminescent centers by majority charge carriers under the action of strong electric fields [246]. Normally, the electron hole pairs are injected from p-type and n-type semiconductors. Therefore it is very common for EL devices to have p-type_intrinsic_n-type (PIN) structures [250-252]. In this study, the EL spectra, over the wavelength range of 300 nm - 900 nm (1.37 eV - 4.13 eV) were measured by a PDS-1 photomultiplier tube (PMT) detector together with a monochromator.

3.6 Current-Voltage (*I-V*) Characterization

The relationship between the electric current in device as a function of the applied voltage is referred to as the current-voltage (*I-V*) characteristic. For light emitting and solar cell devices, this technique can provide information on material resistivity and current conduction mechanisms [53, 253-255]. A probe station system, which consists of an optical microscope, minute contact probes and an HP 4155A precision semiconductor parameter analyzer are used to perform *I-V*

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measurement in our study. The HP 4155A is capable of performing I-V measurements, plotting the device characteristics, extracting device parameters and performing reliability (stress test) evaluation. Fig. 3.7 (a) and (b) show the probe station and the semiconductor parameters analyzer respectively used in our work.

Fig. 3.7 (a) Probe station equipped with an optical microscope and (b) semiconductor parameter analyzer used in this study to perform I-V characterization.

Chapter 4 COMPARISON OF DISPERSION MODELS

IN FITTING SPECTROSCOPIC ELLIPSOMETRY DATA

OF A-SiN_x:H FILMS

4.1 Introduction

Amorphous silicon nitride (a-SiN_x:H) are promising for various optoelectronics applications such as Si photonics [54, 59, 76, 157, 256] and solar cells [257, 258]. They are versatile as their optical properties can be tuned over a wide range by controlling the deposition condition. In the study and application of a-SiN_x:H thin films, it is very important to have a detailed knowledge of their optical properties, which include the index of refraction and absorption coefficient at different photon energies, as well as their thickness. In the literature, the optical properties of a-SiN_x:H thin films have been commonly investigated using the transmission-reflection (TR) spectroscopy, spectroscopic ellipsometry and photothermal deflection spectroscopy (PDS) [30, 32, 202]. Among these techniques, ellipsometry is advantageous as it allows a very precise determination of the film thickness and the complex refractive indices of a-SiN_x:H over a wide energy range [213]. In particular, ellipsometry is well known for its extreme sensitivity to very thin over-layers well below 1 nm thickness [194]. Besides simple thin film layers, ellipsometry is capable of yielding very accurate results for more complicated structures such as multilayers, composite materials, etc [30, 88, 194]. It can also provide very detailed information of the structures such as surface roughness, thin

interface layers and layer compositions [259]. Ellipsometry is an indirect method, i.e. the measured data cannot be converted directly into the optical constants of the sample, and data analysis and fitting using dispersion models must be performed instead. The choice of suitable dispersion models to describe the optical constants of thin films forms a very crucial part of the ellipsometry data analysis. The quality and accuracy of the ellipsometry fitting process is determined by the choice of an appropriate dispersion model that is able to accurately describe the optical constants of the thin films under study over a wide range of energy.

To date, a variety of dispersion relations have been proposed and employed to describe the optical constants of a-Si based materials [194], among which the Tauc-Lorentz (TL) model is the most effective for describing amorphous materials [212]. The TL model however, does not include the defect-induced absorption exponentially decreasing from the band edges. This below bandgap absorption or Urbach tail is an important feature of a-Si based materials and determines many of their characteristics [89]. In this chapter we have investigated TL and two other dispersion models that include the Urbach absorption namely Cody-Lorentz-Urbach (CLU) [218] and Tauc-Lorentz-Urbach (TLU) models [222]. CLU is more flexible than TL since it not only considers the low energy Urbach absorption, but also includes additional transition energies. The other investigated model, TLU, is a modified version of TL model by considering the Urbach tail and the continuity of the first derivative of permittivity. Although TLU and CLU models have more complete definitions of dielectric function, addition of the tail has resulted in more

fitting parameters compared to the TL model. It is not straightforward to determine which model is suitable and appropriate for analyzing the SE data of amorphous materials. On one hand, simpler models with less fitting parameters are easier to fit and can give rise to more unique results. On the other hand, the more complex models can describe the a-SiN_x:H film optical properties more completely but are more challenging to fit to provide unique results.

In this chapter we first review the spectroscopic ellipsometry technique, including its basic principles, instrumentation and data analysis. Then, we present the study of Si rich a-SiN_x:H based on spectroscopic ellipsometry using three different dispersion models namely, Tauc-Lorentz (TL), Cody-Lorentz-Urbach (CLU) and Tauc-Lorentz-Urbach (TLU). To date, there is no detailed study that compares and contrasts the three models when applied in general to amorphous semiconductors. The relatively high absorption coefficient of Si rich films, especially in the low-energy region associated with tail-states, allows a clearer distinction and comparison between dispersion relations with and without considering the Urbach tail. The measured SE data have been fitted to each of these models and the obtained results including the fitting quality, fitted parameters and optical properties are compared and discussed. Based on the fitted results, the suitability of these models to describe the optical properties of a-SiN_x:H will be discussed.

4.2 Spectroscopic Ellipsometry

4.2.1 Overview

Spectroscopic ellipsometry is an optical measurement technique that characterizes the change in polarized light upon light reflection on a sample by measuring the two ellipsometric parameters ψ and Δ as a function of wavelength. ψ and Δ represent the amplitude ratio (ψ) and phase difference (Δ) between p-polarized and s-polarized reflected light waves, which have electric fields polarized parallel and perpendicular to the plane of incidence, respectively. ψ and Δ can be expressed as follows [193, 194]:

$$\rho = \frac{r_p}{r_s} = \tan \psi \cdot e^{i\Delta} \quad (4.1)$$

where r_p and r_s are the s and p polarized reflection coefficients, described independently by Fresnel equations:

$$r_p = \left(\frac{N_1 \cos \theta_0 - N_0 \cos \theta_1}{N_1 \cos \theta_0 + N_0 \cos \theta_1} \right) \quad (4.2a)$$

$$r_s = \left(\frac{N_0 \cos \theta_0 - N_1 \cos \theta_1}{N_0 \cos \theta_0 + N_1 \cos \theta_1} \right) \quad (4.2b)$$

Here N_0 and N_1 are the complex refractive indices of air and the sample respectively and θ_0 and θ_1 are the incident and transmission angles respectively. Equation 4.2 holds for an extremely simple structure consisting of a single layer material in air ambient. For a thin film on substrate or multilayer structures

involving multiple interfaces, the overall s and p polarized reflection coefficients should be used instead, which in turn involves Fresnel reflection and transmission coefficients at individual interfaces [193, 194]. The superposition of multiple light waves introduces interference that should be considered for determination of r_p and r_s (Fig. 4.1). For these structures ψ and Δ are expressed in complicated mathematical relations as a function of layer thicknesses and complex refractive indices [194].

Fig. 4.1 Light reflects and refracts at each interface, which leads to multiple beams in a thin film. Interference between beams depends on relative phase and amplitude of the electric fields. Fresnel reflection and transmission coefficients can be used to calculate the response from each contributing beam

4.2.2 Instrumentation and Measurement

A typical ellipsometry measurement setup is shown in Fig. 4.2. The incident light is linear with both p and s components. The reflected light has undergone amplitude and phase changes for both p and s polarized light, and ellipsometry measures their changes.

Fig. 4.2 Typical ellipsometry configuration, where linearly polarized light is reflected from the sample surface and the polarization change is measured to determine the sample response

The primary building blocks for acquiring ellipsometry data include the following: light source, polarization generator, sample, polarization analyzer, and detector . The polarization generator and analyzer are constructed using optical components that manipulate the polarization: polarizers, compensators, and phase modulators . The polarizer is used to define the incoming polarization and a rotating polarizer after the sample analyzes the outgoing light. The detector converts light to a voltage whose dependence yields the measurement of the reflected polarization. A typical ellipsometer configuration is shown in Fig. 4.3 .

Fig. 4.3 A typical ellipsometer with its main optical components

Although ellipsometric measurements are, by nature, very precise [194], for a detailed investigation of optical properties of thin films, it is very important to acquire accurate and sufficient ψ and Δ data to minimize errors in the final results. One of the ways to achieve this is to acquire data at multiple angles of incidence. The different angles of incidence will lead to changing path length of the probe beam as it travels through the film and hence provide more information about the absorption in the films. Moreover, by performing measurements at different angles of incidence over a wide range, it is possible to acquire data at near pseudo-Brewster angles for each sample. Near this angle the Δ values provide the most sensitive measurement of the sample [194, 262].

4.2.3 Data Analysis

Ellipsometry is an indirect technique, that is, the measured Ψ and Δ quantities do not directly yield the optical properties of the thin films under study. Instead modeling and fitting of the data is required. The most common procedure used to deduce material properties from ellipsometry measurements follows the flow chart in Fig. 4.4 .

Fig. 4.4 Flowchart for ellipsometry data analysis

Data analysis proceeds as follows: After a sample is measured, a model is constructed to describe the sample. The model is used to calculate the predicted response from Fresnel's equations, which describe each material with its thickness and optical constants. If these values are not known, an estimate is given for the purpose of the preliminary calculation. Regression analysis (e.g. Levenberg-Marquardt algorithm) is required because it is extremely difficult to derive an exact

mathematical relation between the sample properties and model unknown parameters. Regression analysis allows all of the measured data to be included when determining the solution. At each regression step, the calculated values are compared to experimental data. The unknown material properties can then be varied to improve the match between experimental and simulated results. To achieve a precise and unique solution, the number of unknown properties should not exceed the amount of information contained in the experimental data. After performing the fit, the Mean Squared Error (MSE), expressed in eq. (4.3) is used to quantify the difference between the experimental and simulated Ψ and Δ results. The unknown parameters are allowed to vary until the minimum MSE is reached. The best fitted parameters in the dispersion relations correspond to the case of lowest MSE.

$$MSE = \left(\frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{cal} - \psi_i^{exp}}{\sigma_{\psi_i}^{exp}} \right)^2 + \left(\frac{\Delta_i^{cal} - \Delta_i^{exp}}{\sigma_{\Delta_i}^{exp}} \right)^2 \right] \right)^{1/2} \quad (4.3)$$

where ψ^{cal} , ψ^{exp} , Δ^{cal} and Δ^{exp} are the fitted and experimental ellipsometric parameters, N is the number of measured Ψ and Δ pairs, M is the number of fit parameters in the optical model, and σ denotes the standard deviation of the measurement in each data point. The MSE is weighted by the error bars on each measured point, therefore, noisy points are weighted less.

4.3 Experiments

The Si rich a-SiN_x:H films were grown by an Applied Material Centura 5200 plasma enhanced chemical vapor deposition (PECVD) system on 8 inch p-type Si <100> substrate at temperature, pressure and RF power of 400°C, 5 Torr and 350 W respectively. The flow rates of the source gases used, SiH₄, NH₃, N₂ and He were set at 120, 38, 3300 and 1250 sccm respectively. The ellipsometric data have been acquired using a rotating analyzer J. A. Woollam variable angle SE in the wavelength range of 270 nm to 1700 nm with a 1 nm step. The angles of incidence were chosen to be 40°, 50°, 60°, 70° and 80°. The fitting of the ellipsometric data was carried out using the WVASE32™ software provided by J. A. Woollam .

4.4 Results

A schematic of the optical model utilized to fit the ellipsometric experimental data of our Si rich a-SiN_x:H sample, including the substrate, the film and a surface roughness layer is shown in Fig. 4.5.

Fig. 4.5 Optical model structure used for fitting SE data of a bulk a-SiN_x:H layer

The optical constants of the c-Si substrate were taken from the literature [263]. The Bruggeman effective medium approximation (EMA) layer defined as 50% void space, and 50% a-SiN_x:H was used to simulate the top surface-roughness layer. The optical constants of the a-SiN_x:H component in the EMA layer were coupled to those of the bulk a-SiN_x:H layer.

The variation film thickness across the sample surface is a common sample non-ideality, which results in partial polarization of the reflected beam has also been considered in our model [264]. We have specified the percentage variation in the film thickness across the probing light beam and let the program fit for this percentage [264].

To determine the optical constants and thickness of our Si rich a-SiN_x:H thin film layer we have chosen three different dispersion models, namely the Tauc-Lorentz (TL), Cody-Lorentz-Urbach (CLU) and Tauc-Lorentz-Urbach (TLU) models.

4.4.1 Tauc-Lorentz Model

A widely accepted and realistic model for the optical functions of amorphous materials is based on the Tauc joint density of states and the Lorentz model for the dielectric response for a collection of single atoms [212]. If only a single transition is considered, then the imaginary part of the dielectric function is given by

$$\varepsilon_2(E) = \begin{cases} \frac{1}{E} \frac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2 + C^2E^2}, & \text{for } E > E_g \\ 0, & \text{for } E < E_g \end{cases} \quad (4.4)$$

where A , E_0 , C and E_g are the amplitude, the peak transition energy, broadening parameter and the optical band gap respectively. The real part ε_1 of the dielectric function is obtained using analytical integration of the Kramers-Kronig relation for $\varepsilon_2(E)$:

$$\varepsilon_1(E) = \varepsilon_{1,\infty} + \frac{2}{\pi} (C.P.) \int_0^\infty \frac{\zeta \varepsilon_2(\zeta)}{\zeta^2 - E^2} d\zeta \quad (4.5)$$

where $(C.P.)$ denotes the Cauchy principal value of the integral [212].

We have successfully fitted the SE data of our a-SiN_x:H sample based on the structure shown in Fig. 4.5 using the TL model to describe the film layer. Fig. 4.6 (a) and (b) plot the spectra of the ellipsometric parameters Ψ and Δ respectively, measured at five incident angles (green lines). The best fitted spectra using TL model are also shown in red lines in the same figure. Except for a slight deviation in the high energy region ($E > 4$ eV), the TL calculated Ψ and Δ are very well matched with the experimental data. Since ellipsometry data acquisition is performed with a constant wavelength resolution, the data points in the higher-energy region of Ψ and Δ are not as closely compacted as the low-energy. The data points are also noisier in the high energy part of the spectra. The WVASE32TM therefore weights this region less in the fitting process.

Fig. 4.6 Experimental (green) and calculated (red) (a) Ψ and (b) Δ of the Si rich $a\text{-SiN}_x\text{:H}$ sample fitted using the TL model

The best-fitted TL parameters obtained for our sample are listed in Table 4.1.

Sample	S12
$R = \text{SiH}_4/\text{NH}_3$	3.16
$\epsilon_I(\infty)$	2.48±0.02
Thickness (nm)	210.3±0.03
A	42.9±0.5
E_n (eV)	4.98±0.02
C (eV)	2.99±0.05
E_g (eV)	2.11±0.003
Surface Roughness Thickness (nm)	4.9±0.03
Thickness Non-uniformity(%)	4.2±0.08
MSE	12.72

Table 4.1.TL fitting parameters obtained for the Si rich a-SiN_x:H thin film layer

4.4.2 Cody Lorentz Urbach Model

The same set of a-SiN_x:H SE data has been fitted by the CLU model where two modifications of the TL expression are applied: the inclusion of an Urbach tail and an additional transition energy as a fitting parameter [218]. These amendments allow us to enhance the capabilities of the analytical model to fit the optical constants of a-Si:H based alloys. The imaginary part of the dielectric function is expressed as [218]:

$$\epsilon_2(E) = \begin{cases} \frac{E_1}{E} \exp\left\{\frac{(E - E_t)}{E_u}\right\}; & \text{for } 0 < E \leq E_t \\ G(E) L(E) = \frac{(E - E_g)^2}{[(E - E_g)^2 + E_p^2]} & \\ \times \frac{AE_0 CE}{(E^2 - E_0^2)^2 + C^2 E^2}; & \text{for } E > E_t \end{cases} \quad (4.6)$$

where $E_t \geq E_g$ is the demarcation energy between the Urbach tail of slope E_u and the band-to-band transitions of optical gap E_g . In Eq. 4.6 the expression for $E > E_t$ includes the product of the Lorentz oscillator function $L(E)$; amplitude: A , resonance energy: E_0 , and width: C and a band edge function $G(E)$. $G(E)$ forces $\epsilon_2(E)$ to assume a desired form for energies just above E_g . In addition, $G(E) \rightarrow 1$ for $E \gg E_g$ so that the desired result $\epsilon_2(E) \rightarrow L(E)$ holds at high energies. E_t is defined so that $\epsilon_2(E)$ is continuous at $E=E_t$ and thus $E_t = E_t L(E_t) G(E_t)$ [218].

The CLU model generalizes the TL approach in that the Urbach tail is added and the function $G(E)$ is defined based on the assumptions of parabolic bands and a constant momentum matrix element with an additional parameter E_p . Here $E_g + E_p$ defines a second transition energy (in addition to E_t) that separates the absorption onset behavior from the Lorentz oscillator behavior. This second transition energy may provide more flexibility than TL expression, however, it can also result in abrupt changes in the slope of the obtained dielectric functions using this model. This is a result of discontinuity at $E=E_t$ in the function $d(\epsilon_2(E))/dE$ in Eq. (4.6).

Fig. 4.7 Experimental (green) and calculated (red) (a) Ψ and (b) Δ of the a-SiN_x:H sample fitted using the CLU model

The real part $\varepsilon_1(E)$ in CLU model is determined from a Kramers–Kronig transformation of $\varepsilon_2(E)$. The best fitted Ψ and Δ graphs for the same set of a-SiN_x:H samples are shown in Fig. 4.7 in red color together with the measured data in green. As can be seen, there is a very good fit between the experimental and calculated

values. Table 4.2 shows the best fitted parameters obtained for the Si rich a-SiN_x:H layer using the CLU model. It is important to note that the error margin for the E_t - E_g parameter is very large compared to the fitted value itself. This is an indication that the results obtained using this model may be inaccurate, which could be a result of too many varying fitting parameters present in the model.

Sample	S12
$R = \text{SiH}_4/\text{NH}_3$	3.16
$\epsilon_l(\infty)$	1.67±0.06
Thickness (nm)	210.3±0.04
A	42.44±1.12
$E_n(\text{eV})$	6.63±0.18
$C(\text{eV})$	8.11±0.37
$E_t - E_g (\text{eV})$	0.35±1.62
$E_p(\text{eV})$	2.04±0.06
$E_g(\text{eV})$	2.18±0.01
$E_u(\text{meV})$	159±4
Surface Roughness Thickness (nm)	5.03±0.03
Thickness Non-uniformity (%)	4.48±0.08
MSE	12.64

Table 4.2 CLU fitting parameters obtained for Si rich a-SiN_x:H thin film layer

4.4.3 Tauc-Lorentz-Urbach Model

Another model examined in this work for fitting the SE data of our Si rich a-SiN_x:H thin film is the Tauc-Lorentz-Urbach (TLU) model [222]. This model has been proposed by adding a low energy exponential absorption edge (Urbach tail) to the TL model and based on the assumption of continuous first derivative of dielectric function [222]. The imaginary part of the dielectric function is defined as [222]:

$$\varepsilon_2(E) = \begin{cases} \frac{1}{E} \frac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2 + C^2E^2}, & \text{for } E > E_c \\ \frac{A_u}{E} \exp\left(-\frac{E}{E_u}\right), & \text{for } 0 < E < E_c \end{cases} \quad (4.7)$$

where the first equation ($E > E_c$) is identical to the TL function and the second equation ($0 < E < E_c$) represents the exponential Urbach tail. The additional parameter E_c denotes the demarcation energy between the Urbach tail transitions and the band-to-band transitions. In Eq. (4.7) E_u is not a fitting parameter and is calculated based on the continuity of the optical functions including their first derivate [222]. Similar to the TL model, ε_I is calculated using the Kramers-Kronig integration. Fig. 4.8 shows the experimental and fitted Ψ and Δ of the sample in green and red respectively. The high energy range discrepancy of TL fitted data is significantly annihilated. Similar results were obtained for the rest of the samples.

Fig. 4.8 Experimental (green) and calculated (red) Ψ and Δ of sample fitted using the TLU model

The best-fitted parameters obtained using the TLU model are summarized in Table 4.3. Unlike the results based on CLU model, the parameters have reasonable error bars.

Sample	S12
$R = \text{SiH}_4/\text{NH}_3$	3.16
$\epsilon_l(\infty)$	2.19 ± 0.03
Thickness (nm)	210.3 ± 0.0
A	54.23 ± 1.01
$E_n(\text{eV})$	5.28 ± 0.03
$C(\text{eV})$	4.1 ± 0.1
$E_c(\text{eV})$	2.47 ± 0.01
$E_g(\text{eV})$	2.18 ± 0.00
$E_u(\text{meV})$	146
Surface Roughness Thickness (nm)	5.02 ± 0.03
Thickness Non-uniformity (%)	4.4 ± 0.1
MSE	12.53

Table 4.3 TLU fitting parameters obtained for Si rich a-SiN_x:H thin film layer. E_u is not a fitting parameter and is calculated based on the formula derived in [222]

4.5 Discussion

After obtaining a good fit, it is important to verify that the obtained fitted parameters are physical and meaningful. The film thickness is one the most important parameters as SE is most sensitive to thickness. Therefore, obtaining accurate thickness values in a model is an indication of the correctness of fitting. In this study the thickness values for each sample obtained using all three models closely match the value that we have obtained independently using a beam profile reflectometer and also expected from the growth time and growth rate of our films are closely matched as shown in Table 4.4.

	a-SiN _x :H Film Thickness
Expected Value from Deposition time and condition	210 nm
Measured by beam profile reflectometer	210 nm
Obtained from ellipsometry data fitting to TL model	210.3±0.03 nm
Obtained from ellipsometry data fitting to CLU model	210.3±0.0 nm
Obtained from ellipsometry data fitting to TLU model	210.3±0.0 nm

Table 4.4 a-SiN_x:H film thickness in sample S12 obtained from ellipsometry (TL, CLU and TLU models), beam profile reflectometer and the one expected from the growth time and condition

The key parameters obtained from the three dispersion formulas are shown in Table 4.5. In this study the optical bandgaps obtained using TL is 2.11 eV and the one deduced using the TLU and CLU models is 2.18 eV. These values are in very good agreement within the experimental error and also comparable values reported for Si rich a-SiN_x:H materials [31, 32, 35, 197, 199]. The obtained Urbach energies using TLU and CLU models are 146 meV and 159 meV respectively, which are within the range reported for similar material [32, 198, 223, 239]. The transition energy obtained using CLU, which is the demarcation energy between the Urbach exponential absorption region and the onset of Tauc absorption [218], has a very large error bar and therefore is considered not as accurate as the one obtained using TLU model. The surface roughness and thickness non-uniformity percentage resulted from the three models are found to be consistent.

Parameters	Tauc-Lorentz Model	Cody-Lorentz-Urbach Model	Tauc-Lorentz-Urbach Model
Thickness (nm)	210.3±0.03	210.3±0.04	210.3±0.0
Transition Energy (eV)	--	$E_t=2.53\pm1.62$	$E_c=2.47\pm0.01$
E_g (eV)	2.11±0.00	2.18±0.01	2.18±0.00
Surface Roughness Thickness (nm)	4.9±0.03	5.03±0.03	5.02±0.03
Thickness Nonuniformity(%)	4.2±0.08	4.48±0.08	4.4±0.1
MSE	12.72	12.64	12.53

Table 4.5 Key parameters obtained for S12 using TL, CLU and TLU dispersion models

The real and imaginary parts of the refractive index are calculated for the three models and plotted in Fig. 4.9. (a) and (b). The real parts of the refractive indices deduced from the three models are consistent except a deviation of less than 10% in the high-energy region. The n spectra shown in Fig. 4.9 (a) are in agreement with Lelievre et. al report for their Si rich a-SiN_x:H samples [197]. As for the extinction coefficient shown in Fig. 4.9 (b), there is an obvious difference in the low-energy region between the two models that include the Urbach tail (CLU and TLU models) with the one obtained using TL model. This is conformable with the definition of these models, since TL model assumes the absorption to be zero

below bandgap while in CLU and TLU models there is an exponential absorption below the transition energy [212, 218, 222].

Fig. 4.9 (a) Real and (b) imaginary parts of the refractive index of a-SiN_x:H thin film

One of our main objectives is to examine whether the Urbach-tail addition to the TL model has enhanced the goodness of the fit of the data. The MSE is the first criterion for evaluating the quality of the fit, with a smaller MSE giving rise to a better fit. In this work however, no significant change is observed in the MSE values obtained using TL, CLU and TLU models (Tables 4.1.to 4.3). To analyze and clearly reveal the quality of the fit using the three models with and without the Urbach tail, we have compared the resultant residues (the differences between experimental and calculated Ψ and Δ). Such plots can provide very useful information about the goodness of fit at specific wavelength range. The Ψ and Δ residue spectra obtained from the three models are compared in Fig. 4.10. Only those spectra at the incident angles where there are distinct differences in the residues among the models used are shown. Ideally, the residue should be a noisy spectrum around zero without any trend behavior. According to Fig. 4.10., there is a significant improvement in high energy range using the TLU and CLU models.

Comparison of dispersion models in fitting spectroscopic ellipsometry data of a-SiN_x:H films

Comparison of dispersion models in fitting spectroscopic ellipsometry data of a-SiNx:H films

Fig. 4.10 The difference between calculated and experimental data of the sample S12, using the TL (black) and TLU (blue) and CLU (red) models. Only the Ψ and Δ spectra at those incident angles where there are obvious differences are shown

4.6 Conclusion

In conclusion, we have compared three different dispersion relations, Tauc-Lorentz, Cody-Lorentz-Urbach or Tauc-Lorentz-Urbach, used to fit the SE data of a Si rich a-SiN_x:H thin film. We have successfully fitted the measured data in the energy range 0.7 eV to 4.8 eV using all the three models. The surface roughness layer and thickness non-uniformity are considered in the model to obtain an accurate fitting. The fitted parameters obtained using the three models are discussed, compared together. Based on this comparative study, we believe that the Tauc-Lorentz-Urbach model is more suitable than the Tauc-Lorentz model to characterize this Si rich a-SiN_x:H film as it describes the absorption coefficient more accurately with the incorporation of the Urbach tail absorption.

rich a-SiN_x:H film as it describes the absorption coefficient more accurately with the incorporation of the Urbach tail absorption. This is reflected in the decrease of discrepancy between the experimental and calculated data. The Tauc-Lorentz-Urbach model is also more suitable than the Cody-Lorentz-Urbach model, mainly since it has less fitting parameters and results in the fitted parameters with smaller error bars and therefore more distinctive results.

Chapter 5 INVESTIGATING

PHOTOLUMINESCENCE AND OPTICAL PROPERTIES OF A-SiN_x:H THIN FILMS

5.1 Introduction

a-SiN_x:H thin films have potential applications in optoelectronic devices. Their optical bandgap can be tuned over a wide range by controlling the films stoichiometry [32, 59, 201]. The ease of injecting current into this material also renders it advantageous for electroluminescence applications [54, 76-79, 84]. Due to its attractive properties, a-SiN_x:H has been investigated as an efficient light emitting material in Si microphotonics utilized in single layer films as well as multilayer structures[50, 76, 79, 160, 265]. In this chapter we report the fabrication and characterization of a-SiN_x:H thin films using the plasma enhanced chemical vapor deposition (PECVD) technique. By varying the precursor gas flow ratio, a range of stoichiometry has been achieved. This study serves to identify the optimum deposition condition to grow efficient light emitting a-SiN_x:H material to be used ultimately for the fabrication of our electroluminescent devices. The knowledge of materials emission characteristics, its thickness and absorption coefficient is necessary to estimate their light emitting efficiency [32, 247]. Moreover, the optical properties, including complex refractive index and emission properties reflect essentially the density of states and thus their analysis is one of the most effective tools for understanding the electronic structure of amorphous

materials. Although its PL properties has been widely investigated [29, 31, 32, 34, 35, 57, 59, 149, 156, 197, 199, 266, 267], a-SiN_x:H absorption coefficient has been studied less extensively using techniques such as transmission-reflection (TR) method [30, 32] and ellipsometry [197, 213]. The simplicity and usefulness of spectroscopic ellipsometry and its advantages compared to other techniques such as TR, photo thermal deflection spectroscopy (PDS) was reviewed in the previous chapters. In the same chapter, the effectiveness of Tauc-Lorentz-Urbach (TLU) dispersion model to fit the ellipsometry data of Si rich a-SiN_x:H films, compared to the Tauc-Lorentz (TL) and the Cody-Lorentz-Urbach (CLU) models was also presented. TLU model takes into account the low energy exponential absorption edge of the material. By utilizing this model we can also determine important optical parameters such as Urbach energy, which is not deducible by fitting the data to TL model. Moreover, as opposed to CLU model, using TLU we do not face the problem of parameters with large error bars. In this chapter, we have reported our detailed investigation of the a-SiN_x:H optical properties by fitting their ellipsometry data using TLU model. We have then correlated the obtained results to the photoluminescent (PL) characteristics. Taking into account the PL intensities, films thicknesses and their absorption coefficients at the PL excitation wavelength, we have determined the most efficient a-SiN_x:H sample amongst the series for light emitting applications. The corresponding deposition condition has been used for the fabrication of light emitting multilayer devices, which will be presented in the next chapter.

In addition to controlling of the stoichiometry in a-SiN_x:H thin films, thermal annealing of such films is also a common approach to increase their emission efficiency [34, 35, 154, 155]. We have therefore, performed an annealing process in N₂ ambient for one hour in the temperature range of 500°C to 1000°C on the samples. The effect of annealing temperature on the structural, optical and emission properties have been investigated and presented for one of the a-SiN_x:H samples in this chapter.

5.2 Experiments

The a-SiN_x:H films used in this study were grown by an Applied Material Centura 5200 PECVD system on 8 inch p-type Si <100> substrate at temperature, pressure and RF power of 400°C, 5 Torr and 350 W respectively. Four different stoichiometries have been grown by changing the SiH₄ flow rate from 40 sccm to 120 sccm while keeping the NH₃, N₂ and He flow rates constant at 38, 3300 and 1250 sccm respectively. In Table 5.1, the samples are listed together with their corresponding gas flow ratios.

Sample Label	SiH ₄ (sccm)	$R = \text{SiH}_4/\text{NH}_3$
S12	120	3.16
S9	90	2.37
S6	60	1.58
S4	40	1.05

Table 5.1 a-SiN_x:H sample labels and their corresponding gas flow ratios

Thermal annealing process was carried out using a furnace in N₂ ambient. FTIR spectroscopy was performed to investigate the chemical bonds of the deposited films. Each spectrum was taken as the average over 32 scans with a 4 cm⁻¹ wavenumber resolution from 400 cm⁻¹ to 4000 cm⁻¹. For PL measurement a 0.1 mW laser diode with 371 nm wavelength and a Hamamatsu multi channel plate photo multiplier tube were used as the excitation source and detector respectively. The spectra measured at room temperature were corrected for the optical response of the system. The ellipsometric data have been acquired using a rotating analyzer J. A. Woollam variable angle spectroscopic ellipsometry in the wavelength range of 270 nm to 1700 nm with a 1 nm step. The angles of incidence were chosen to be 40°, 50°, 60°, 70° and 80°. Measurement at multiple angles of incidence helps to reduce the noise in the fitted parameters, improve their confidence limits and eliminate multiple solutions. In addition, the choice of a wide range of angles ensures that for each wavelength at least one pair of ψ and Δ is most sensitive to the model parameters [268]. The fitting of the ellipsometric data was carried out using the WVASE32TM software. The difference between experimental and calculated ellipsometric data was quantified by mean squared error (MSE) based on Levenberg–Marquardt algorithm.

5.3 Investigating As Deposited a-SiN_x:H Films

To investigate the effects of SiH₄ flow ratio $R = \text{SiH}_4/\text{NH}_3$, on the chemical bonding structure in a-SiN_x:H, we have performed FTIR spectroscopy. The results, after eliminating the interference effects by a baseline subtraction are shown in Fig. 5.1. The peaks in the spectra are at around 830 cm⁻¹, 1180 cm⁻¹, 2180 cm⁻¹ and

3350 cm⁻¹, which are attributed to Si-N stretching, N-H bending, Si-H stretching and N-H stretching bonds respectively [34, 35, 43, 223, 269, 270] as indicated in the figure. It is readily observed that by increasing R , the Si-H stretching mode continuously increases, whereas the N-H stretching bond decreases. This is due to the higher ratio of Si-H species to N-H species in the chamber during the reaction process as a result of increasing R . It has been reported that there was an increase in the Si concentration in such films prepared under a higher silane flow ratio [35]. Our results indicate that an increasing number of N atoms are bonded to Si atoms for samples prepared with a lower R [35].

Fig. 5.1 FTIR spectra of the a-SiN_x:H samples with the chemical bonds indicated

To obtain the complex refractive index of the a-SiN_x:H films we have performed ellipsometry measurements. The ellipsometry experimental data have been fitted to an optical model consisting of: a c-Si substrate, the a-SiN_x:H film and a surface

roughness layer (Fig. 4.1). The a-SiN_x:H thin film is described by the Tauc-Lorentz-Urbach dispersion formula. Fig. 5.2 (a) and (b) show the experimental (green) and fitted (red) Ψ and Δ of S6. As can be seen, the spectra measured and simulated at all the five incident angles match very well for the entire measured energy range, which is an indication of a successful fit. The not so perfect match in the high-energy region ($4.6 \text{ eV} < E < 4.7 \text{ eV}$) is probably due to the fact that the number of data points (measured at wavelength resolution of 1 nm) is relatively small and compared to the rest of the spectrum and therefore, this part of the data is weighed less in the fitting procedure by WVASE32. Similar very good fits between the Ψ and Δ experimental and simulated spectra have also been obtained for the other samples.

Fig. 5.2 Experimental (green) and calculated (red) Ψ and Δ of sample S6 fitted using the TLU model. The quality of the fit can be readily seen from the conformity between the experimental and fitted curves at all the five incident angles

The best-fitted TLU parameters obtained from fitting the SE data of the $a\text{-SiN}_x\text{:H}$ samples are summarized in Table 5.2. The low MSE values and error margins associated with each parameter (within 5% of the parameter value) are quantitative indications of a successful fit.

	S12	S9	S6	S4
$R = \text{SiH}_4/\text{NH}_3$	3.16	2.37	1.58	1.05
$\epsilon_i(\infty)$	2.19±0.03	1.58±0.04	1.07±0.04	1.43±0.13
Thickness(nm)	210.3±0.0	184.4±0.0	142.1±0.0	103.1±0.0
A	54.23±1.01	67.5±1.6	74.8±1.5	136±7
$E_n(\text{eV})$	5.28±0.03	7.32±0.09	9.38±0.09	8.41±0.56
$C(\text{eV})$	4.1±0.1	7.1±0.2	4.8±0.1	7.6±1.2
$E_c(\text{eV})$	2.47±0.01	2.76±0.01	3.82±0.03	5.36±0.17
$E_g(\text{eV})$	2.18±0.00	2.41±0.00	3.14±0.01	4.55±0.12
$E_u(\text{meV})$	146	172	322	392
Surface Roughness Thickness (nm)	5.02±0.03	4.94±0.04	4.63±0.04	6.77±0.07
Thickness Non-uniformity (%)	4.4±0.1	5.2±0.1	5.6±0.1	5.8±0.1
MSE	12.53	14.42	9.73	9.96

Table 5.2 TLU best fitting parameters for a-SiN_x:H films described in

Table 5.1

From Table 5.2, we can observe a consistent decrease in the optical bandgap (E_g) and transition energy (E_c) with R . According to Robertson's calculations the bandgap decreases as more Si is introduced in the a-SiN_x:H network, owing to the presence of Si-Si σ and σ^* bands which raises the valence band and lowers the conduction band [198]. The decreasing trend of the transition energy (E_c) with R is also in agreement with the bandgap change. As the valence and conduction bands separate with increasing bandgap, band to band absorptions start to occur at larger

energies as well, [36, 40, 89] leading to a larger demarcation energy between tail state and band to band state absorptions that is defined as E_c in TLU dispersion relation [222].

Another important parameter obtained from the ellipsometry study is the Urbach energy E_u defined as the exponential slope of the absorption coefficient spectrum associated with the localized bandtail transitions [89]. According to previous studies on a-SiN_x:H, E_u increases with N concentration as a result of broadening of the tail states due to topological disorder [32]. Such a trend is clearly seen in our obtained E_u values as well (Table 5.2).

Fig. 5.3 (a) and (b) shows the energy-dependant refractive index (n) and extinction coefficient (k) of the a-SiN_x:H films, corresponding to different gas ratios R . As the gas flow ratio is increased, both n and k increase. The refractive indices of a-SiN_x:H films have been reported to monotonically increase with decreasing x , as the films approach from stoichiometric nitride to Si rich nitride [197, 223] For our samples, it is expected that increasing R will lead to more Si being incorporated into the films and hence account for the larger refractive indices seen. Cai et al have correlated the n increase in their rapid thermal annealed a-SiN_x:H films to a decrease in the total bonded hydrogen concentration [271]. Similar correlation can be seen according to the FTIR results in this study that show an increased number

of nitrogen atoms back bonded to Si in the films grown with a lower R which means less Si-H bonds in the films.

Fig. 5.3 (a) Real and (b) imaginary parts of refractive indices of a-SiN_x:H films obtained using the TLU model from ellipsometry data fitting

The absorption coefficient $\alpha(E)$ was calculated from the obtained $k(E)$ using Eq. (2.1) and is shown in Fig. 5.4. In the same plot we have indicated the transition energies E_c for the samples. The E_c for S4 is outside the energy range plotted and hence not shown. E_c can be easily identified in the $\alpha(E)$ graph where the slope is

changed, since it is the demarcation energy at which the definition of ε_2 changes in the TLU dispersion relation (see Eq. (4.7)).

Fig. 5.4 Absorption coefficient of a-SiN_x:H films in logarithmic scale.

The transition energy E_c are indicated for the samples

Fig. 5.5 shows the PL spectra of the a-SiN_x:H samples measured at room temperature. The PL intensity rapidly increases from almost zero at $R = 1.05$ to a maximum at $R = 1.58$ and then decreases after that.

Fig. 5.5 PL characteristic of a-SiN_x:H films with different chemical compositions measured at room temperature

The negligible PL intensity of sample S4 is likely attributed to the fact that near stoichiometric nitrides are inherently not efficient in luminescence [34, 197]. Its larger bandgap of 4.55 eV, indicates its near stoichiometric nature and accounts for the very low absorption at the excitation wavelengths (Fig. 5.4), which also contributes to decrease the PL. Two systematic trends are observed in the PL spectra by increasing the silane flow ratio:

1-The peak PL wavelength increases, from 607 nm at $R = 1.58$ to 757 nm at $R = 3.16$. The PL blue shift is a consequence of an increase in the bandgap as deduced from our ellipsometry results. Similar increase in the bandgap and PL peak energy with N concentration in a-SiN_x:H films has been reported previously [32, 35, 80,

161, 199]. The increasing trend of E_g , E_c and the PL peak energy with R is shown in Fig. 5.6.

Fig. 5.6 Optical bandgap E_g and transition energy E_c obtained from the TLU model for the a-SiN_x:H thin films as a function of gas flow ratio R . PL peak energy is shown in the same graph

2- The PL bands' full width at half maximum (FWHM) decreases from ~240 nm at $R = 1.58$ to ~200nm at $R = 2.37$ and 3.16. For the samples with PL spectra not completely detected using our PL system, we have estimated the FWHM the left half of the corresponding spectrum which were completely obtained (Fig. 5.5). The PL band broadening has also been confirmed from our ellipsometry results and the increasing trend of E_u with R . According to previous studies, at lower R due to the incorporation of more nitrogen in the films, the localized tail states are widened [32, 40, 199]. Broadening the tail states accounts for the increasing trend of the PL

width [32]. Fig. 5.7 presents the dependence of both E_u and the PL FWHM on the Silane flow ratio R of our samples.

Fig. 5.7 PL FWHM and Urbach energy as a function of R

The possible mechanisms for PL in a-SiN_x:H are the radiative recombination between bandtail states [32, 199, 200, 239], or within Si quantum dots (either in amorphous or crystalline form) in the Si nitride matrix [54, 59, 161]. Radiative recombination in defect states deep in the bandgap may also contribute to light emission of a-SiN_x:H material [31]. In this study, we have not observed any indication of nanocrystalline Si presence in our films by X-ray diffraction measurements results (not reported here). This could be due to either their very small size or low density that is not detectable or simply because they do not exist in our films. High resolution transmission electron microscopy has not revealed a

trace of Si nanocrystals in the films either. Therefore we have excluded the possibility that the light emission is attributed to Si nanocrystals in the SiN matrix.

Having obtained the absorption coefficient of the films, we have compared the films' PL efficiency by correcting the integrated PL intensity by the factor $(1-\exp(-\alpha d))$, where d is the film thickness, and α is the absorption coefficient at the PL excitation wavelength (a-SiN_x:H Thin Films 371 nm $\sim$ 3.34 eV) to account for the amount of excitation light absorbed. The results are shown in Fig. 5.8 where it is seen that the optimum R ratio to achieve a high PL efficiency is 1.58.

Fig. 5.8 PL efficiency as a function of gas flow ratio R

5.4 Investigating the Effect of Thermal Annealing

In this section we present the results and discussion of thermal annealing experiments performed on the sample S6. The results of this sample were chosen to represent the investigation of annealing treatment on a-SiN_x:H samples discussed in the previous section.

Fig. 5.9 shows the FTIR spectra of the as-deposited and annealed samples. There is a strong peak located in the range of 720 cm⁻¹ to 1100 cm⁻¹ that corresponds to Si-N absorption. The absorption band centered near 1040 cm⁻¹ is proposed to be a shoulder on the main Si-N stretching band near 840 cm⁻¹ arising from Si-N bond with a H atom backbonded to Si atom [202, 272]. The peak at ~1140 cm⁻¹ is attributed to N-H bending bonds [35]. The intensity of the N-H bands continuously decreases with increasing temperature which indicates that H is desorbing from the films. We also note an increase in the absorption of Si-N stretching bond with annealing temperature which is in agreement with previous studies [154, 267]. The intensity of Si-H stretching bond detected at ~2180 cm⁻¹ [35] is unchanged up to the annealing temperature of 700°C but decreases at higher temperatures. It can be deduced from these results that during annealing, excess N dangling bonds formed from the release of H atoms bonded with Si-Si bonds to generate two stable Si-N bonds, i.e., $2\text{N-H} + \text{Si-Si} \rightarrow 2\text{Si-N} + \text{H}_2 \uparrow$ [267].

Fig. 5.9 FTIR spectra of as-deposited and annealed a-SiN_x:H sample S6

The optical properties of all the a-SiN_x:H films were studied using ellipsometry. The experimental ψ and Δ were fitted using the TL model, from where their thickness, optical bandgap and complex refractive indices were determined. The best fitted key parameters together with the resultant MSE are shown in Table 5.3.

Annealing Temperature (°C)	As-deposited	500	600	700	800	900	1000
Thickness (nm)	143±0.03	142±0.03	140±0.03	136±0.03	135±0.03	131±0.03	143±0.02
A	95.5±0.4	102.4±0.2	102.4±0.2	121.8±0.5	100.7±0.1	100.7±0.1	99.7±0.1
$E_n(eV)$	10.8±0.01	11.9±0.03	12.1±0.03	12.7±0.06	11.5±0.02	12.4±0.02	10.8±0.01
$C(eV)$	6.3±0.1	7.2±0.1	8.7±0.1	10.0±0.2	5.7±0.01	10.6±0.01	6.4±0.01
$E_g(eV)$	2.71±0.01	2.92±0.00	2.95±0.00	3.21±0.01	2.96±0.00	2.89±0.01	2.56±0.0
Surface Roughness Thickness (nm)	3.5	2.2	1.9	1.6	1.3	1.7	3.2
MSE	11.6	11.1	9.6	9.6	11.0	10.5	7.5

Table 5.3 Best fitted TL model parameters obtained for as deposited and annealed a-SiN_x:H films

According to Table 5.3, the film thickness continuously decreases with annealing temperature. The optical bandgap first increases with annealing temperature up to 700°C and then decreases continuously at higher temperatures.

Fig. 5.10 shows the real part of the refractive indices of the as-deposited and annealed a-SiN_x:H films obtained from the ellipsometry fitting results. We observe a continuous increase in n for the films with increasing annealing temperature,

which becomes more significant for samples annealed at 900°C and 1000°C. This increase could be correlated to a decrease in the films thicknesses and the subsequent increase in the films density at higher temperatures due to H desorption. At 900°C annealing temperature, the Si-H and N-H bonds are broken and H is exhausted from the material as confirmed from FTIR spectra in Fig. 5.9. Meanwhile Si and N atoms may diffuse a short distance to bond together and consequently the film becomes denser [159] leading to an increase in n .

Fig. 5.10 Real part of the refractive indices of the as-deposited and annealed a-SiNx:H films

Photoluminescence experiments were performed for as-deposited and annealed samples and the results are plotted in Fig. 5.11. The spectra are broad which is characteristic of amorphous semiconductors. Although the PL intensity varies with annealing temperature, the profiles are generally similar before and after annealing indicating that the origin of emission has not fundamentally evolved. Previous

studies have shown that the emission mechanism in annealed a-SiN_x:H films is transformed after a certain temperature due to creation of Si clusters in the films [35]. In the present experiments however we have not observed the existence of such particles in the high resolution transmission electron micrograph of the films even after annealing at 1000°C. The FTIR results also suggest the reconstruction of the Si-N bonds by thermal annealing.

Fig. 5.11 PL spectra of as-deposited and annealed a-SiN_x:H measured at room temperature

Fig. 5.12 The PL efficiency evolution with annealing temperature in a-SiN_x:H films

Fig. 5.12 shows the PL efficiency as a function of annealing temperature after correcting for the integrated absorption at the excitation wavelength. The initial increase in PL efficiency (up to 700°C) could be due to the improvement of the structure and the diminishing number of nonradiative centers after annealing [35]. The efficiency however degrades for films annealed at higher temperatures which could be a consequence of increased Si dangling bonds acting as nonradiative centers due to desorption of H from Si atoms [273-275] as confirmed by the FTIR results.

The values are obtained by dividing the corresponding integrated intensities by $[1 - \exp(-\alpha d)]$, where α is the absorption coefficient at the excitation wavelength (371nm) and d is the film thickness.

Apart from the PL intensity, we can also observe the PL peak changes after annealing at different temperatures as shown in Fig. 5.13: it increases up to annealing temperature of 700°C and then continuously decreases for higher temperatures. We attribute this change to the bandgap evolution as reported in Table 5.3.

Fig. 5.13 PL peak energy and optical bandgap as a function of the annealing temperature

Based on the consistent trend observed in the variation of PL peak energy and the optical bandgap with annealing temperature (Fig. 5.13), we suggest that the PL is a

result of radiative recombination between localized bandtail states [29, 32, 33, 59, 156, 197, 198].

5.5 Conclusion

In summary, the optical properties and PL of a group of a-SiN_x:H films deposited by the PECVD technique with different stoichiometries have been investigated. To obtain the optical properties, spectroscopic ellipsometry measurements were performed in a wide energy range and at various incident angles to result in accurate experimental values of Ψ and Δ . We have successfully fitted the measurement data using the Tauc-Lorentz-Urbach model. Compared to the previously used Tauc-Lorentz model this model takes into account the below bandgap absorption (Urbach tail) in the parameterization of the dielectric function. This will consequently result in more accurate knowledge of the optical properties. Furthermore, using this parameterization model, another important physical parameter, the Urbach energy can be obtained in addition to the optical bandgap. The obtained optical properties are in good agreement with PL characteristics. Such detailed knowledge of optical and emission properties of a-SiN_x:H is very important in considering a-SiN_x:H for optoelectronic applications. The continuous decrease of optical bandgap with Si concentration obtained from ellipsometry results is in agreement with the PL red shift. This is an indication of the light emission originating from bandtail radiative recombination. The bandtail width broadening with N concentration, indicated in Urbach energy and PL linewidth increase also indicates the PL originating from photogenerated carriers recombining in bandtails.

Taking into account the amount of excitation absorption and integrated PL intensity for each sample, the sample with the silane flow ratio of $R= 1.58$ is found to have the highest PL efficiency. We have used this growth condition to fabricate our light emitting multilayers and electroluminescent devices, which will be presented in the next chapter.

We have also studied a-SiN_x:H films deposited using the PECVD technique and annealed at different temperatures. The structural, optical and PL characteristics of the films have been investigated as a function of the annealing temperature. From FTIR spectroscopy measurements we have observed that Si-N bond concentration increases with temperature whereas the N-H bonds continuously decrease. The Si-H bond decreases only at high temperatures. The films become denser and refractive index increases after annealing at high temperatures. The PL efficiency is found to be enhanced by annealing up to 700°C but degrades at higher temperatures attributed to creation of nonradiative centers as a result of increasing Si dangling bonds in the films. The change in the PL peak energy is a result of a similar change in the optical band gap and the emission is proposed to be due to radiative recombination in the localized bandtail states before and after annealing.

Chapter 6 **A-SiN_x:H/SiO₂MULTILAYERS**

6.1 Photoluminescence and Optical Properties

6.1.1 Introduction

In line with the realization of a light source in Si micro-photonics, utilizing systems containing low-dimensional Si have been proposed where the electronic properties of free carriers are modified by quantum confinement effects. Porous Si and Si quantum dots embedded in a dielectric matrix are examples of such nanostructured systems [54, 60, 64, 276]. Porous Si lacks the desired structural stability and is not fully compatible with standard complementary metal oxide semiconductor manufacturing. As for Si quantum dots embedded in a SiO₂ matrix, the controlling of the Si nanostructures' surface, size, homogeneity and concentration to achieve desirable luminescence properties are difficult challenges to overcome [66, 68, 69]. More importantly, it is difficult to inject electrical current efficiently into the light emitting nanostructures through highly insulating materials such as SiO₂ [71, 72, 74, 277]. Replacing SiO₂ with Si₃N₄ as the dielectric matrix material will lower the barrier height for the injection of electron hole pairs due to the smaller bandgap of Si₃N₄. However, even for Si nanostructures embedded in Si₃N₄, the electron hole pairs need to be transported through the thick insulating nitride barrier. Another approach is to utilize a-Si:H and its alloys in multilayer structures which also benefit from quantum confinement of carriers to enhance their emission properties [76, 77, 80, 82]. Multilayers have the advantages of better reproducibility in fabrication and more structural stability compared to porous Si. In addition, unlike

Si nanostructure systems which are difficult to reproduce, the layer thicknesses and compositions can be precisely controlled, thanks to the availability of advanced deposition techniques [75, 76, 78, 191, 278]. This will result in tunable optical properties and emission characteristics for multilayer structures [75, 76, 78, 191, 278]. Moreover, with respect to their utilization in electroluminescence devices, multilayer structures allow electron-hole pairs to be injected efficiently through the very thin barrier layers, which is a big advantage over other low dimensional Si systems [76, 77, 86].

In this section, the growth and characterization of a-SiN_x:H/SiO₂ multilayer structures are reported. Their optical and emission properties are studied in detail using photoluminescence (PL) and spectroscopic ellipsometry. To study the effect of well layer thickness on the PL and optical properties, a-SiN_x:H/SiO₂ multilayers with a fixed SiO₂ thickness of 10 nm and two well layer thicknesses of 3 nm and 6 nm are fabricated on crystalline Si substrates. Bulk single layers of a-SiN_x:H and SiO₂ materials have also been fabricated with the same growth conditions as those used for multilayers to serve as a reference. To achieve high PL intensities, the gas flow ratio for a-SiN_x:H layers deposition was chosen to be the optimum value of $R=1.58$ as deduced from our earlier investigations presented in Chapter 5. The complex refractive indices of the well and barrier layers are precisely determined using ellipsometry, and their variation with the well layer thickness is discussed and correlated to the changes in PL characteristics.

6.1.2 Multilayer Fabrication

a-SiN_x:H/SiO₂ multilayers have been grown using the plasma enhanced chemical vapor deposition (PECVD) technique. For a-SiN_x:H material deposition, SiH₄, NH₃, N₂ and He have been used with flow rates of 60, 38, 3300 and 1250 sccm respectively. The conditions correspondent to a silane flow ratio of $R = \text{SiH}_4/\text{NH}_3 = 1.58$, which has been shown in Chapter 5 to give rise to the most efficient photoluminescence. As for SiO₂ deposition, N₂O and SiH₄ with flow rates of 2000 sccm and 40 sccm were used. The detailed deposition conditions of the well and barrier layers including the Radio frequency (RF) power, chamber pressure and substrate temperature are shown in Table 6.1.

Material	Substrate Temperature (°C)	Chamber Pressure (Torr)	RF Power (Watts)
a-SiN _x :H	400	5	350
SiO ₂	400	3	270

Table 6.1 PECVD conditions for the growth of the a-SiN_x:H well and SiO₂ barrier layers in the multilayer structures.

Two a-SiN_x:H/SiO₂ multilayers structures were grown, with the SiO₂ barrier layer thickness fixed at 10 nm and the a-SiN_x:H well layer width set at 3 and 6 nm. The two well layers thicknesses were precisely controlled by adjusting the deposition times to 2 sec and 4 sec respectively. The deposition time of the SiO₂ barrier layer was 1.6 sec. To avoid intermixing of the very thin layers, the RF power was

stopped after each layer deposition and the chamber was evacuated before depositing the subsequent layer. In total 10 periods of well and barrier layers were grown for each sample (Table 3.3). Two SiO₂ buffer layers of 50 nm each have been deposited on the top and bottom of the multilayer structures. A schematic of multilayer structures fabricated in this study showing the number of layers and the thicknesses are shown in Fig. 3.3. A single layer of the a-SiN_x:H well and SiO₂ barrier material have also been grown with the same deposition conditions as the multilayer structures, but with a longer deposition time to serve as references for comparison. Table 6.2 shows the labels of the samples and their detailed structures, including the number of layers and thickness values.

Sample Label	Number of Periods	Well Layer Thickness (nm)	Barrier Layer Thickness (nm)
M3	10	3	10
M6	10	6	10
S1	--	140	--
S2	--	--	100

Table 6.2 The structural information of the two multilayer samples M3 and M6 and the two single layer samples S1 and S2

Figs. 6.1 and 6.2 show the cross sectional TEM pictures of the samples M3 and M6. The a-SiN_x:H and SiO₂ layers can be clearly distinguished with their abrupt interfaces, indicating minimum intermixing of the layers. Despite that the layers

are very thin they are noted to be very uniform in terms of their thickness. From the TEM micrograph, the well and barrier layers thicknesses are deduced to be about 3 nm and 6 nm respectively, close to the expected values estimated from the deposition rates and times of the layers.

Fig. 6.1 (a) and (b) High resolution (HR) TEM image of the sample M3 with a-SiN_x:H well layer thickness of 3 nm under different scale bars. The layers in darker color in the figure are the a-SiN_x:H layers

Fig. 6.2 (a) and (b) High resolution (HR) TEM image of the sample M6 with a-SiN_x:H well layer thickness of 6 nm under different scale bars. The layers in darker color in the figure are the a-SiN_x:H layers

6.1.3 Results and Discussion

To obtain the optical properties of individual layers in our multilayer samples we have used the spectroscopic ellipsometry. For ellipsometry data analysis, it is generally very challenging to obtain accurate results for films that are extremely thin in a multilayer structure. For the multilayers structures fabricated in this work, not only are the layers very thin, but the number of layers is also very large. Therefore, it is immensely crucial to acquire very accurate experimental data set that contains as much information about the samples as possible. To accomplish that, each sample in this work was measured at five incident angles of 40°, 50°, 60°, 70° and 80°. The different angles of incidence will lead to changing path length of the probe beam as it travels through a film and hence provide more information about the absorption in the films. Moreover, by performing a variable angle of incidence in a wide range, it is possible to acquire data at near pseudo-Brewster angles for each sample. Near this angle the Δ values provide the most sensitive measurement of the sample [193]. In this study, a wavelength resolution of one nanometer in a wide range from 270 nm to 1700 nm, with 50 analyzer revolution per wavelength was chosen for the ellipsometry data acquisition. The measurements were performed at different spots on each sample to verify their consistency.

The next step is to build an appropriate model based on the optical properties and structures of the samples. We have developed a model in which a layer is added to represent each individual layer in the structure on top of a Si substrate. In the fitting process, the thicknesses and the optical parameters of all the well layers, and

likewise all the barrier layers, are coupled together to minimize the number of fitting variables and avoid possible high correlations. This is physically justified due to the fact that the deposition time and the growth conditions are identical for all the well layers, and likewise for the barrier layers. In order to avoid getting into local minima, the initial parameters for the a-SiN_x:H and SiO₂ materials were determined by the ones obtained from the fitting of the data of the corresponding single reference layers.

To describe the SiO₂ barrier layers the Cauchy model has been applied. As for the a-SiN_x:H well layers, we have used the Tauc-Lorentz (TL) and Tauc-Lorentz-Urbach (TLU) models. As reported in Chapters 4 and 5, these two models fit the ellipsometry data of our a-SiN_x:H material well and yield physically meaningful parameters useful for the analysis of these materials. For the case of multilayers however, utilizing the TLU model for describing the well a-SiN_x:H materials results in a number of multiple solutions rather than a unique solution. This could be due to the complexity of the multilayer structure, involving many additional parameters in the fitting as a result of the existence of both well and barrier layers. The fact that the complex refractive indices of the well a-SiN_x:H and barrier SiO₂ layers are not too significantly distinct can also contribute to the difficulty in the data fitting for the multilayer structures as compared to single layers. Furthermore, it was not possible to clearly reject some of the solutions with convincing physical reasoning. Moreover, it was found that using the more complex TLU model resulted in a high correlation among the fitted parameters. Therefore, we have not

used the TLU model to describe the a-SiN_x:H well layer in our multilayer structures, and the TL model has been used instead.

Figs. 6.3 and 6.4 show respectively the Ψ and Δ measured for the sample M3 and M6 at all five incident angles from 40° to 80° in green color. The best-fitted data, using the corresponding developed optical models is shown in each figure in red color. It is apparent that the fitted Ψ and Δ match very well the experimental data.

Fig. 6.3 (a) Ψ and (b) Δ measured at five incident angles for the multilayer sample M3 in green color. The red color curves are the corresponding fitted results

Fig. 6.4 (a) Ψ and (b) Δ measured at five incident angles for the multilayer sample M6 in green color. The red color curves are the corresponding fitted results

To quantitatively evaluate the quality of the fit, we use the mean squared error (MSE) as defined in Eq(4.3). The key fitted parameters obtained from the samples together with their error margins are summarized in Table 6.3.

Fitting Parameters	M3	M6	S1	S2
Thicknesses (nm)				
a-SiN _x :H Well layer	3.06±0.057	5.13±0.05	140.96±0.02	--
SiO ₂ Barrier layer	11.44±0.05	11.74±0.04	--	105.74±0.02
SiO ₂ Buffer layer	48.48±0.20	52.31±0.13	--	--
Tauc-Lorentz Parameters				
E_g (eV)	4.39±0.21	3.29±0.02	3.06±0.02	
C (eV)	0.79±2.21	1.36±0.22	1.65±0.083	
E_0 (eV)	13.22±1.14	11.32±0.52	7.96±0.09	
A	77.49±10.2	55.03±5.91	42.12±1.3	
e_1	0.90±0.41	1.44±0.22	1.96±0.04	
Cauchy Parameters				
A	1.44±0.00	1.45±0.00		1.45±0.00
B	0.005±8e-5	0.006±7e-5		0.004±4e-5
MSE	19.06	20.17	8.964	8.311

Table 6.3 The key fitted parameters obtained from SE data analysis of single layer a-SiN_x:H, S1, single layer SiO₂ S2 and the multilayer structures, M6 and M3

The fitted ψ and Δ conforming to the experimental data (Figs. 6.3 and 6.4) together with the low MSE values (Table 6.3) clearly show qualitatively and quantitatively the high quality of the fit. The accuracy of the results obtained can also be confirmed through the thickness of the well and barrier layers deduced, which are

consistent with what we have obtained from the TEM micrographs as summarized in Table 6.4. Besides, the obtained thickness values from the ellipsometry fitting results including the well and barrier layers are also very well matched to the expected values according to the growth conditions.

	a-SiN _x :H Well Layer Thickness Expected from Deposition time and Conditions	a-SiN _x :H Well Layer Thickness Measured using TEM	a-SiN _x :H Well Layer Thickness Obtained from Ellipsometry Results	SiO ₂ Barrier Layer Thickness Expected from Deposition time and Conditions	SiO ₂ Barrier Layer Thickness Measured using TEM	SiO ₂ Barrier Layer Thickness Obtained from Ellipsometry Results
M3	3.3 nm	3-4 nm	3.06 nm	10 nm	10-11 nm	11.44 nm
M6	6.6 nm	5-7 nm	5.13 nm	10 nm	10-11 nm	11.74 nm

Table 6.4 The well and barrier layer thicknesses, as expected from the growth conditions, measured from TEM graphs and obtained from ellipsometry fitting

Fig. 6.5 compares the real part of the refractive indices of the SiO₂ barrier layers in the multilayer samples M6, M3, and that deduced for the SiO₂ bulk layer. Although the results are obtained independently from individual data sets, the resultant refractive index n spectra of the SiO₂ layers in the different samples are very close to each other and within 2% of error. As the deposition conditions of these SiO₂ barrier layers are fixed across the multilayers and the bulk single layer, the

similarity of the n spectra is an indication of the accuracy of the results obtained as well as the good reproducibility in the growth of the SiO₂ layer. It also suggests that there was minimum intermixing of the layers in the multilayer structures as previously deduced from the TEM results.

Fig. 6.5 Real part of the refractive index of the SiO₂ layers in the M3 and M6 multilayer structures, and in the S2 single layer

As shown in Table 6.3, the Tauc-Lorentz bandgaps deduced are 3.06 eV, and 3.29 eV and 4.39 eV for the bulk material, samples M6 and M3, respectively. There is a continuous increase in the bandgap when the thickness of the a-SiN_x:H is reduced from the bulk layer to the thin 6 nm and 3 nm in the multilayer structures. The increase in optical bandgap with thickness has been previously observed in different amorphous multilayer structures [76, 80, 184, 185, 187, 279, 280]. Although The blue shift of the optical band gap is often taken as a proof of the

quantum confinement of carriers in multilayer structures [76, 80, 184, 185, 187], possible interface layers may also contribute in observation of such a trend [279, 280]. To verify whether the optical bandgap blue shift in this study is truly dominated by the effect of size rather than interface layers, we refer to the TEM graphs in Figs 6.1 and 6.2 showing abrupt interfaces in between the a-SiN_x:H well and SiO₂ barrier layers samples M3 and M6 respectively. In addition to TEM, we have used the spectroscopic ellipsometry, which is a powerful technique for the study of such thin interface layers [196, 281]. The ellipsometry data analysis also confirms very low possibility of interface layers existence in our multilayer structures. Therefore, it is likely that the change in the optical bandgap could be due to the quantum confinement of carriers as a result of reducing the thickness in a-SiN_x:H layers [76, 80, 184, 185, 187].

Fig. 6.6 shows the real (n) and imaginary part (k) of the bulk a-SiN_x:H layer, and the a-SiN_x:H well layers in the multilayer structures. The change in n may be attributed to the quantum size effect, which has been shown to lower the dielectric constant of crystalline Si when its film thickness is reduced [282]. Yoo et al. have also obtained similar results experimentally, which is in agreement with a theory based on the surface polarization effect [283]. As for the k spectra, a decrease in the absorption with reducing thickness of the a-SiN_x:H layer can be clearly seen, which is in agreement with the increasing Tauc-Lorentz bandgap as seen earlier on.

Fig. 6.6 (a) Real and (b) imaginary parts of the refractive index of a-SiN_x:H in the single layer S1 and the two multilayer structures M3 and M6 with different well layer thicknesses

Fig. 6.7 shows the photoluminescence (PL) results obtained from the bulk a-

SiN_x:H and the multilayer samples. The SiO₂ barrier layer material, sample S2, has been independently measured and found to have zero PL, therefore the PL observed from the multilayer samples is associated with a-SiN_x:H well layers. The spectra are generally broad that is associated with the amorphous nature of the a-SiN_x:H. The PL intensity is observed to be slightly stronger for the sample M6 as compared to the bulk layer, despite that the overall thickness of SiN_x:H (that is, summing up all the individual well layers) in M6 is less than that in the bulk material. The increase in the PL intensity can be ascribed to the spatial localization of electron hole pairs in the well layers, due to the nanometric thickness of these layers and to the presence of the barrier layers which prevents carrier diffusion among the well layers [187, 284].

Fig. 6.7 Room Temperature PL spectra of the bulk (S1) and multilayer samples (M3 and M6) with different well layer thicknesses

Fig. 6.8 PL spectra obtained from (a) S1 bulk a-SiN_x:H S1, (b) the multilayer sample M6 and (c) the multilayer sample M3. Each spectrum is deconvoluted to two Gaussian peaks shown in green and red color and their summation is plotted in blue color

To have an in-depth understanding of the emission characteristics of a-SiN_x:H and their evolution with the thickness, each emission spectrum is deconvoluted into two Gaussian peaks as demonstrated in Fig. 6.8. The details of the peak positions, their full width at half maximum (FWHM) and integrated intensity are summarized in Table 6.5.

	S1	M6	M3
Peak Wavelength 1 (nm)	511.4±1.88	502.62±1.75	482.42±2.71
FWHM1 (nm)	124.80	107.48	105.58
Integrated Intensity 1	2.3±1.7	2.5±0.8	0.71±0.2
Peak Wavelength 2 (nm)	598.6±14	586.1± 8.02	610±3.02
FWHM 2 (nm)	222.03	227.50	234.74
Integrated Intensity 2	12.7±2.3	12.8±1.3	7.06±0.5

Table 6.5 Key parameters of the two Gaussian peaks that have been used to fit the PL spectra of the a-SiN_x:H bulk (S1) and multilayer samples (M3 and M6) with different well layer thicknesses

The lower PL peak energy (peak 1 in Table 6.5), does not demonstrate any trend with thickness. Theoretical model has predicted that the peak position of defect-related PL in a-SiN_x:H depends only on the defect energy level; it is almost fixed for a given defect, and will not be easily controlled [160, 161]. According to Deshpandeh model for PL in a-SiN_x:H, the peak at the lower energy could be a result of radiative recombination between N₄⁺ and N₂⁰ levels [31]. Therefore, we attribute the low-energy PL peak of our multilayer and single layer samples to the

radiative recombination of defect states residing in the bandgap of a-SiN_x:H. The high-energy peak wavelength however, continuously decreases with the a-SiN_x:H well layer thickness in the multilayer samples. This is in agreement with the decrease in the optical bandgap of a-SiN_x:H with well layer thickness according to the SE data analysis. The high energy peaks in the PL spectra originate from radiative recombination between bandtail states in the a-SiN_x:H layers and its blue shift with the decrease in thickness is the result of bandgap widening which can be associated with possible quantum confinement effect [76, 80, 184, 185, 187].

6.1.4 Conclusion

In summary, we have fabricated two sets of a-SiN_x:H/SiO₂ multilayer structures with a-SiN_x:H well layer thicknesses of $d = 3$ and 6 nm and a fixed SiO₂ barrier layer of 10 nm. The layer thicknesses were precisely controlled by adjusting the deposition condition and time. We have compared their PL and optical properties to those of a single bulk a-SiN_x:H layer. The optical properties were obtained by fitting the spectroscopic ellipsometry data measured at five incident angles from 40° to 80° in a wide wavelength range of 270 nm to 1700 nm. The data sets were fitted to an optical model describing a-SiN_x:H and SiO₂ layers using the Tauc-Lorentz and Cauchy dispersion relations respectively. The complex refractive indices of the individual layers were obtained after successfully fitting the data to the developed models. The optical bandgap of the a-SiN_x:H layers were found to increase in the multilayer structures compared to that of the bulk a-SiN_x:H layer. Comparing the two multilayer samples, the optical band gap is blue shifted when the well layer

thickness is reduced from 6 nm to 3 nm, which could be attributed to the quantum confinement effect. The room temperature PL measured from the samples can be deconvoluted into two Gaussian peaks. The high-energy peak which demonstrates a blue shift consistent with the optical bandgap obtained from ellipsometry results, is attributed to the radiative recombination between bandtail states. The low-energy peak, which is unchanged in the bulk material and the two multilayer samples may be originated from radiative recombination in defect states residing in the bandgap of a-SiN_x:H.

6.2 Electroluminescence

6.2.1 Introduction

In the previous section, we have reviewed the advantages of a-Si based multilayer structures as potential candidates for Si microphotonics light emitting applications. To date, multilayer structures consisting of alternating ultra-thin layers of a-Si and dielectric films such as SiO₂ have received intensive research attention in aspects of both photoluminescence (PL) and electroluminescence (EL) [71, 75, 81, 82, 180, 181, 183, 189, 254, 278, 285]. Although a-Si/SiO₂ multilayers are efficient light emitters under optical injection, they are not suitable for fabricating electrically excited devices due to the large band offset between SiO₂ and a-Si. To reduce the band offset between the barrier and well layers, Si₃N₄ was proposed to replace SiO₂ in such multilayer structures [76, 86]. To fabricate electroluminescent devices based on a-Si multilayers, a vertical-current-injection method, similar to the one

utilized in III-V multi quantum well lasers, has been conventionally used [78, 79, 86, 183, 265]. Although this injection method is efficient for III-V based devices, where both well and barrier layers are semi-conducting, it is not efficient for a-Si based multilayer devices in which the barrier material is highly-insulating. The SiO₂ or Si₃N₄ barrier layers will lead to poor transport of carriers across the device. A further disadvantage of these conventional structures employing vertical-current-injection scheme is the large difference of carrier densities in the individual quantum well [286]. In a conventional multilayer device, electrons and holes are injected into the wells in the direction perpendicular to the well surfaces. The mobility of electrons is much higher than that of holes, and thus electrons move faster than holes under a given bias voltage. Therefore, the carrier density is higher in quantum wells near the anode than those near the cathode [83]. To achieve a high efficiency EL, in this project we have proposed a novel structure where the electric current is injected laterally and parallel to the multilayer structure instead of perpendicular to it [84]. In this way, the current mainly flows only through the well layers and not the barrier layers, and hence the injection process is expected to be much more efficient. In this chapter, we describe the structure of the proposed device, its fabrication and characterization results that include current-voltage and room temperature EL. To serve as a comparison with our proposed lateral device, a multilayer structure device based on the conventional vertical current injection has also been fabricated and studied.

6.2.2 Device Structure

For the study of a-SiN_x:H multilayer structure electroluminescent, a lateral injection device structure has been fabricated where the current flows parallel to the plane of multilayer. The electrodes are designed to be on the two sides of the luminescent multilayer. In this section the process steps involved in the fabrication of the lateral and vertical injection device structures will be presented.

The major process steps of the lateral device fabrication are shown in Fig. 6.9. The 3D schematic and the top view of the completed lateral EL device are shown in Fig. 6.10 (a) and (b) respectively. The process started with 8-inch Si substrates followed by the deposition of a 50 nm thick layer of buffer SiO₂ that served as an isolator between the substrate and the subsequent layers. This is important to prevent any possible current leakage between the electrodes and the Si substrate. The active luminescent region comprises the multilayer structure that consists of 20 alternating layers of 6 nm a-SiN_x:H and 5 nm SiO₂ was then grown followed by a 50 nm thick SiO₂ passivation layer on the top. The a-SiN_x:H and SiO₂ materials were grown using PECVD technique with the deposition condition as reported earlier in the section 6.1.2 To enhance the emission efficiency of multilayer samples, a series of annealing treatments have been performed in N₂ ambient for one hour with annealing temperature in the range of 500°C to 1100°C. The annealing temperature of 1000°C was found to be the most efficient condition and was therefore used for the fabrication of EL devices. The active region was defined

by deep UV lithography including 550 nm of polymer photo resist material coating, exposure using a 248 nm stepper and reactive ion etching through the multilayer to expose the bottom buffer oxide. We used CF_4 with flow rate of 35 SCCM as etchant gas, chamber pressure is 40 mTorr and RF power is 400W. The etching rate was about 10Å per second. The challenge is to stop the etching process right before the bottom SiO_2 buffer layer without leaving any multilayer material un-etched. Therefore the dry etch process was divided into two or three stages after which the etched area was examined using an interferometer. After each dry etching stage, the thickness of the SiO_2 buffer layer deposited immediately on top of the Si substrate was measured to assure that no over etch has occurred. If the thickness was found to be larger than the initial SiO_2 buffer layer thickness, another dry etch stage was performed.

The active region was then patterned into interdigitated finger structures to have a large surface area for emission. The photoresist material is then stripped in a two-step wet etching process using Diluted HF (10 secs) and sulfuric-peroxide mixture (10 minutes). After each lithography step, the wafers were inspected under optical microscope to ensure that the patterned area is clean from particles and defects. Afterwards, a layer of 180 nm poly-Si was deposited at temperature of 540°C using low pressure chemical vapor deposition (LPCVD). To form a PIN structure two steps of lithography were used to carry out high dose implantation of boron and phosphorous for p^+ and n^+ electrode formation. The polysilicon electrodes n and p implantations have been carried out using a Varian implanter, with concentration of $4 \times 10^{15} \text{ cm}^{-3}$ and energies of 60 and 24 keV respectively. The emission window was

formed by etching the poly-Si on top of the active region. Finally, the fabricated devices were annealed in N₂ ambient for 1 hour at 700 °C for dopant activation.

Fig. 6.9 Major process steps to fabricate the lateral device (i) Deposition of the multilayer active region (ii) Active region patterning and etching (iii) Deposition of poly-Si and implantation to form p^+ and n^+ electrode (iv) Poly-Si patterning and etching to form a grating-like structure on the active region

Fig. 6.10 (a) a 3D schematic and (b) top view of the lateral EL device

Fig. 6.11 (a) shows the cross sectional TEM picture of the multilayer used for the EL devices, indicating abrupt interfaces between the a-SiN_x:H and SiO₂ layers and minimum intermixing of the layers. The well and barrier layers are also noted to be very uniform. From the TEM micrographs, the well and barrier layer thicknesses are deduced to be about 6 and 5 nm respectively, almost equal to the expected values estimated from the deposition rates and times for the layers. Fig. 6.11 (b) shows the TEM micrograph of the device with the multilayer etched to the bottom oxide layer and heavily doped *n* and *p* type poly Si deposited at the two sides for current injection parallel to the layers.

Fig. 6.11 TEM graph of (a) the multilayer and (b) the side-view of the fabricated EL device. Poly Si electrodes are deposited perpendicular to the multilayer for lateral current injection

For the fabrication of the vertical injection device, 8-inch Si substrates were implanted with phosphorous to be used as the negative bottom electrode. Subsequently, the multilayer structure was deposited layer-by-layer using the PECVD technique with the same conditions as the lateral devices, after which multilayer deposition the top poly-Si electrode was deposited using LPCVD and implanted by boron. It should be highlighted that unlike the lateral device, the 50 nm SiO₂ buffer layers on top and bottom of the multilayer are not deposited for the fabrication of vertical devices. Finally, the multilayer and poly-Si were patterned and etched down to substrate forming square and circle patterns with various areas. The key process steps are shown in Fig. 6.12.

Fig. 6.12 Key process steps to fabricate the vertical device (i) multilayer deposition (ii) poly Si deposition and implantation with boron and (iii) gate patterning

6.2.3 Results and Discussion

Fig. 6.13 (a) and (b) show the current-voltage relation of the lateral and vertical device structures respectively. The lateral device has a low leakage current under reverse bias ($\sim 0.25 \text{ kA/m}^2$ at -10 V that indicates good rectifying characteristics of the device. The forward bias I - V relation of the lateral device in lower voltages (corresponding to $V < 4 \text{ V}$) is characterized by an exponential behavior, predictable due to the junction nature of the p-i-n structure. At higher voltages however the I - V behavior is dominated by the current transport through the a-SiN_x:H i-layer. To identify the conduction mechanism in our a-SiN_x:H material we have investigated the possibility of Poole Frenkel (PF) and Fowler Nordheim (FN) mechanisms in our materials by comparing their J-E relations with those experimentally obtained from the EL devices.

Fig. 6.13 I-V characteristic of the (a) lateral and (b) vertical EL devices

Poole Frenkel (PF) is commonly identified as one of the dominant conduction mechanisms in *a-SiN_x:H* materials. One would expect a linear $\ln(J/E)$ vs. $E^{1/2}$ plot, J and E being the current density and electric field respectively, if the transport is dominated by the PF model. Such relation in our measurement results is however

far from linear and hence suggests that the PF model is not able to explain the transport mechanism in our EL device.

Another model to describe the current transport in a-SiN_x:H is the Fowler-Nordheim tunneling mechanism, in which the J - E relation is given by [106, 118, 126, 127]:

$$J = C_{FN} E^2 \exp \left(\frac{-E_{FN}}{E} \right) \quad (6.2)$$

where the pre-exponential (C_{FN}) and exponential (E_{FN}) factors are functions of free electron mass and the barrier height in silicon nitride [106, 118, 126, 127]. To observe the possibility of the FN tunneling mechanism in the films studied we have plotted $\ln (J/E^2)$ vs. $1/E$ in Fig. 6.14. From the linear nature of the data one can infer that FN tunneling could be responsible for conduction at E field range corresponding to $V > 4V$.

50Fig. 6.14 $\ln(J/E^2)$ vs. $1/E$, calculated from I - V measurement of the EL device

To estimate the relative electrical injection efficiency of vertical and lateral devices, current densities at identical applied voltages have been compared. A significant improvement of more than nine orders of magnitude has been observed in the laterally injected device at a voltage of 10 V. This can be attributed to the absence of highly resistive barrier layers in the current path [84].

The electroluminescence was detectable at the lowest current of 1 mA, at an applied voltage of 11.5 V. Therefore we estimate this value to the turn on voltage of our electroluminescent device. No EL was observed under the reverse bias condition. Fig. 6.14 shows the measured EL spectra of the device under various pumping conditions. The spectra correspond well to the observed color of the emission. They are composed of a main peak at ~660 nm and a shoulder peak at a

shorter wavelength of ~560 nm. The inset shows the integrated EL intensity and its increase with increasing current. The shape and peak positions of the spectra are independent of the current and therefore the applied field. This indicates that the EL is a result of radiative recombination of electron hole pairs injected from the *n* and *p* poly Si rather than due to impact ionization[287]. In the impact ionization process, as the current passing through the device increases, the EL intensity increases abruptly and its peak wavelength and width may change [71, 72, 74]. When the tunneled electron-hole pairs in the active material recombine radiatively, however, the EL spectrum does not change in shape, and its intensity increases linearly with current density passing through the device [287].

Fig. 6.15 EL spectra of a typical device under various electric currents.

The inset shows the integrated EL intensity as a function of the applied current

Fig. 6.15 shows the PL spectra measured from as deposited and 1000 °C annealed multilayer samples without the poly Si gates. The increase in the PL efficiency

observed could be due to the diminishing of nonradiative centers after annealing. The similar broadness and peak positions (at ~660 nm) of the EL and PL spectra in Figs 6.14 and 6.10 suggest that both electrically and optically pumped emission mechanisms can be related to the same origin. The shorter wavelength peak in the PL spectrum is however not as distinct as in the EL. This could be a result of interference effects due to the poly Si gates that only exist in the EL sample. It is worth noting that no PL or EL was observed from a control SiO₂ sample with identical deposition conditions. Therefore, the observed light emission is attributed to radiative recombination of electron hole pairs in the thin a-SiN_x:H well layers.

Fig. 6.16 PL spectra of as deposited and 1000°C annealed samples. The intensity has increased by more than four times after annealing.

6.2.4 Conclusion

In conclusion, we have demonstrated light emission from an a-SiN_x:H/SiO₂ multilayer structure grown by the plasma enhanced chemical vapor deposition technique. The multilayer is sandwiched between two heavily doped *n* and *p* poly-Si regions to form a PIN structure. Electric current is injected parallel to the multilayer structure and as a result flows mainly through only the well layers but not the barrier layers. Therefore, compared to the normal current injection, the potential barrier is substantially minimized and a higher current density can be injected at a lower voltage.

Chapter 7 CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

In this project multilayer structures consisting of very thin layers of a-SiN_x:H sandwiched between SiO₂ were designed, fabricated, characterized and subsequently utilized to fabricate electroluminescent devices for Si photonics applications. a-SiN_x:H has been chosen as the light emitting material in our multilayer structure due to its efficient luminescent characteristics and the ability to control its optical bandgap and emission wavelength over a wide energy range as a function of the Si concentration. We have demonstrated that light emitting efficiency is enhanced in a-SiN_x:H/SiO₂ multilayer structures compared to single layer a-SiN_x:H thin film, and that the emission wavelength can be tuned by controlling the a-SiN_x:H layer thickness. To fabricate light emitting devices, a novel method of current injection where the electric field is applied parallel to the plane of multilayer structure has been used. This has been shown to be more efficient compared to electrical injection where the electric field is applied normal to the plane of the multilayer structure.

The a-SiN_x:H films have been grown on c-Si substrate using the plasma enhanced chemical deposition (PECVD) technique with a gas mixture of SiH₄, NH₃, N₂ and He. The gas flow ratio $R = \text{SiH}_4/\text{NH}_3$ has been varied in the range of $R = 1.05$ to $R = 3.16$ to give rise to films with different stoichiometry. They have been characterized using the photoluminescence (PL) and spectroscopic ellipsometry

techniques to determine the deposition condition that gives rise to films with the highest light emitting efficiency. To obtain their complex refractive indices from the ellipsometry data, three different dispersion models Tauc-Lorentz (TL), Cody-Lorentz-Urbach (CLU) and Tauc-Lorentz-Urbach (TLU) have been considered and compared. TLU was chosen to fit the ellipsometry data of single layer a-SiN_x:H since it takes into account the low-energy exponential absorption edge (Urbach tail) in amorphous materials, which is not considered in the TL model. It also results in fitting parameters with smaller error bars compared to the CLU model. After fitting the ellipsometry data, the films thicknesses and their absorption coefficients at the PL excitation energy have been obtained and used together with PL intensity to determine their emission efficiency. The gas flow ratio of $R= 1.58$ was found to give rise to the highest PL efficiency and has been used for the subsequent fabrication of a-SiN_x:H/SiO₂ multilayer structures and light emitting devices in this study.

To study the light emission characteristics and optical properties of multilayer structures, two samples consisting of 20 alternative layers of a-SiN_x:H (well) and SiO₂ (barrier) have been fabricated using the PECVD technique with the SiO₂ layer thickness fixed at 10 nm and a-SiN_x:H thicknesses at 3 nm and 6 nm. The thicknesses were precisely controlled by adjusting the deposition time. A single layer of a-SiN_x:H (140 nm thick) with the same deposition condition but a longer deposition time has also been grown to serve as a comparison. The samples were characterized by the spectroscopic ellipsometry and PL techniques.

To determine the absorption coefficient and the optical bandgap of the a-SiN_x:H layers in the multilayer structures from the ellipsometry data, an optical model has been utilized where the Tauc-Lorentz and Cauchy dispersion models describe the well and barrier layer materials respectively. The measured ellipsometry data have been successfully fitted to this model from which the well and barrier layer thicknesses and their complex refractive indices were determined. The thicknesses of the well and barrier layers were closely matched to those measured from transmission electron micrographs. The optical bandgap of the a-SiN_x:H well layers obtained as a fitting parameter of the Tauc-Lorentz dispersion model are found to increase from 3.29 eV to 4.39 eV when the thickness decreases from 6 nm to 3 nm. These values are higher compared to the 3.26 eV optical bandgap obtained for single layer a-SiN_x:H. We have attributed this to the quantum confinement effect.

The room temperature photoluminescence efficiency of the multilayer samples is enhanced compared to the single layer material and is attributed to the spatial confinement of carriers in the very thin layers of a-SiN_x:H. The PL spectra have been deconvoluted to two Gaussian peaks. The high-energy peak, which demonstrates a blue shift at smaller a-SiN_x:H thickness, is consistent with the change in the optical bandgap obtained from ellipsometry results. It is attributed to the radiative recombination between bandtail states. The low-energy peak, which is unchanged in the bulk material and the two multilayer samples may be originated from radiative recombination in defect states residing in the bandgap of a-SiN_x:H.

We have designed and fabricated efficient light emitting devices where the a-SiN_x:H/SiO₂ multilayer structures are sandwiched between two heavily doped *n* and *p* poly-Si regions to form a PIN structure. Electric current is injected parallel to the multilayer structure and as a result flows mainly through only the well layers but not the barrier layers. Therefore, compared to the normal current injection, the potential barrier is substantially minimized and a higher current density can be injected at a lower voltage.

7.2 Future work

Based on the work presented here, several recommendations for future works are outlined in this section.

7.2.1 Time-resolved and Temperature Dependent Photoluminescence

Investigation of Multilayer Structures

Studying the luminescence lifetime of a-SiN_x:H/SiO₂ multilayer structures as a function of well layer thickness will help to establish a better understanding of the light emitting mechanisms in such structures [80, 288]. This will serve to validate the possibility of quantum confinement effect inferred from the steady state PL and optical bandgap results.

The temperature dependent PL studies of the films and nanostructures can also be used to identify the contribution of possible excitation and emission mechanisms in the PL spectra. It would therefore be a useful study to measure the temperature dependent PL spectra of single layer and multilayer structures [32, 36, 37, 89, 198, 289, 290].

7.2.2 Investigating Quantum Confinement in Multilayer Structures

In this project, we have demonstrated the change in the photoluminescence characteristics of a-SiN_x:H/SiO₂ multilayer structures as a function of the well layer thickness. Further study is required to investigate effect of quantum confinement in the multilayer structures.

Moreover, towards their application as EL devices it is interesting to investigate the effect of a-SiN_x:H well layer thicknesses and compositions on the EL properties as well [78, 86]. Besides, as the electric current is driven efficiently through only the a-SiN_x:H well layers in the laterally injected devices [84], it is also possible to investigate various devices by increasing the SiO₂ thicknesses without compromising the EL intensity. Increasing the SiO₂ thickness may result in reduced coupling of the electron wavefunctions among the adjacent wells and hence a stronger confinement of carriers in the a-SiN_x:H layers.

7.2.3 Photonic Crystal Structures

There is a significant discrepancy between the internal efficiency and relatively poor external efficiency of light emitting devices. A large fraction of the generated light is never emitted from the material, but is trapped by total internal reflection [291]. This limitation applies to our EL devices based on a-SiN_x:H/SiO₂ multilayer structures as well. Therefore we propose to utilize photonic crystal patterns, which have been shown to be effective for improving the light extraction efficiency [292] to further improve our device performance. By controlling the optical modes of the periodic arrays via varying their structural parameters, the intensity and profile of spontaneous emission can be efficiently modulated [71, 293].

Author's Publications

Kamyab, L., Rusli, "Comparison of dispersion models in fitting spectroscopic ellipsometry data of a-SiN_x:H films." Ready for submission to Journal of Applied Physics.

Kamyab, L., Rusli, Yu M. B., Ding, L., & Lo, G. Q. "Electroluminescence from amorphous-SiN_x:H/SiO₂ multilayers using lateral carrier injection." Applied Physics Letters 98(6): 061105-3.

Kamyab, L., Rusli, Yu M. B. "Visible Photoluminescence and Electroluminescence from a-SiN_x:H/SiO₂ Multilayers With Lateral Carrier Injection", IEEE Proceeding, Group IV Photonics Conference, Beijing September 2010.

Kamyab, L., Rusli, Yu M. B. "Electroluminescence from a-SiN_x:H/SiO₂ Multilayers Using Lateral Carrier Injection", Global Photonics Conference, Singapore December 2010.

Kamyab, L., Rusli, Yu, M. B., He, L., & Dua, M. (2009). "Optical Properties and Visible Room Temperature Photoluminescence of Amorphous Silicon Rich Silicon Nitride in SiO₂/SiN_x Quantum Well Structures." International Journal of Nanoscience.

Kamyab L., Rusli., Yu, M. B., He, L., & Dua, M. "Investigation of Optical Properties and Photoluminescence of Amorphous Silicon Carbide in a-SiC/Si₃N₄ Quantum Well Structures Fabricated by PECVD Technique," ECS Transactions - Vienna, Austria, vol. 25, 2009.

Bibliography

- [1] "International Technology Roadmap for Semiconductors (ITRS)
<http://www.itrs.net/links/2009ITRS/Home2009.htm>."
- [2] C. T. Sullivan, "Optical waveguide circuits for printed wire-board interconnections," USA, 1989, pp. 92-100.
- [3] K. W. Jelley, G. T. Valliath, and J. W. Stafford, "High-speed chip-to-chip optical interconnect," *IEEE Photonics Technology Letters*, vol. 4, pp. 1157-1159, 1992.
- [4] L. Pavesi, "Will silicon be the photonic material of the third millenium? *," *Journal of Physics: Condensed Matter*, vol. 15, pp. R1169-R1196, 2003.
- [5] J. W. Goodman, F. J. Leonberger, S.-Y. Kung, and R. A. Athale, "OPTICAL INTERCONNECTIONS FOR VLSI SYSTEMS," *Proceedings of the IEEE*, vol. 72, pp. 850-866, 1984.
- [6] G. T. Reed and C. E. Jason Png, "Silicon optical modulators," *Materials Today*, vol. 8, pp. 40-50, 2005.
- [7] R. A. Soref, "Silicon-based optoelectronics," *Proceedings of the IEEE*, vol. 81, pp. 1687-1706, 1993.
- [8] R. A. Soref and J. P. Lorenzo, "Silicon guided-wave optics," *Solid State Technology*, vol. 31, pp. 95-8, 1988.
- [9] B. Jalali and S. Fathpour, "Silicon photonics," *Journal of Lightwave Technology*, vol. 24, pp. 4600-4615, 2006.
- [10] A. O. Splett, T. Zinke, B. Schueppert, K. Petermann, H. Kibbel, H.-J. Herzog, and H. Presting, "Integrated optoelectronic waveguide detectors in SiGe for

- optical communications," in *Photodetectors and Power Meters II*, San Diego, CA, USA, 1995, pp. 224-234.
- [11] L. Ansheng, R. Haisheng, M. Paniccia, O. Cohen, and D. Hak, "Net optical gain in a low loss silicon-on-insulator waveguide by stimulated Raman scattering," *Optics Express*, vol. 12, 2004.
- [12] K. Lionel C, "Silicon microphotronics," *Applied Surface Science*, vol. 159-160, pp. 8-13, 2000.
- [13] O. Boyraz and B. Jalali, "Demonstration of a silicon Raman laser," *Optics Express*, vol. 12, 2004.
- [14] S. M. Csutak, J. D. Schaub, W. E. Wu, and J. C. Campbell, "High-speed monolithically integrated silicon optical receiver fabricated in 130-nm CMOS technology," *IEEE Photonics Technology Letters*, vol. 14, pp. 516-18, 2002.
- [15] C. E. Png, S. P. Chan, S. T. Lim, and G. T. Reed, "Optical Phase Modulators for MHz and GHz Modulation in Silicon-On-Insulator (SOI)," *J. Lightwave Technol.*, vol. 22, p. 1573, 2004.
- [16] A. Irace, G. Breglio, and A. Cutolo, "All-silicon optoelectronic modulator with 1 GHz switching capability," *Electronics Letters*, vol. 39, pp. 232-3, 2003.
- [17] B. Li, Z. Jiang, X. Zhang, X. Wang, J. Wan, G. Li, and E. Liu, "SiGe/Si Mach-Zehnder interferometer modulator based on the plasma dispersion effect," *Applied Physics Letters*, vol. 74, pp. 2108-2109, 1999.
- [18] L. Pavesi, S. V. Gaponenko, and L. Dal Negro, *Towards the first silicon laser*. Dordrecht ; Boston: Kluwer Academic Publishers, 2003.

- [19] L. Dal Negro, M. Cazzanelli, N. Daldosso, Z. Gaburro, L. Pavesi, F. Priolo, D. Pacifici, G. Franz², and F. Iacona, "Stimulated emission in plasma-enhanced chemical vapour deposited silicon nanocrystals," *Physica E: Low-dimensional Systems and Nanostructures*, vol. 16, pp. 297-308, 2003.
- [20] L. Pavesi, "A review of the various approaches to a silicon laser," in *Photonics Packaging and Integration III*, San Jose, CA, USA, 2003, pp. 206-220.
- [21] F. Giorgis, G. Ambrosone, U. Coscia, S. Ferrero, P. Mandracci, and C. F. Pirri, "Structural and optical properties of a-Si_{1-x}C_x:H grown by plasma enhanced CVD," Netherlands, 2001, pp. 204-8.
- [22] L. Wang, J. Xu, T. Ma, W. Li, X. Huang, and K. Chen, "The influence of the growth conditions on the structural and optical properties of hydrogenated amorphous silicon carbide thin films," *Journal of Alloys and Compounds*, vol. 290, pp. 273-278, 1999.
- [23] M. B. Yu, Rusli, S. F. Yoon, S. J. Xu, K. Chew, J. Cui, J. Ahn, and Q. Zhang, "Hydrogenated nanocrystalline silicon carbide films synthesized by ECR-CVD and its intense visible photoluminescence at room temperature," *Thin Solid Films*, vol. 377-378, pp. 177-181, 2000.
- [24] W. A. Nevin, H. Yamagishi, M. Yamaguchi, and Y. Tawada, "Emission of blue light from hydrogenated amorphous silicon carbide," *Nature*, vol. 368, pp. 529-31, 1994.
- [25] J. Cui, Rusli, S. F. Yoon, M. B. Yu, K. Chew, J. Ahn, Q. Zhang, E. J. Teo, T. Osipowicz, and F. Watt, "Effects of microwave power on the structural and emission properties of hydrogenated amorphous silicon carbide deposited by

- electron cyclotron resonance chemical vapor deposition," *Journal of Applied Physics*, vol. 89, pp. 2699-2705, 2001.
- [26] J. Cui, Rusli, S. F. Yoon, E. J. Teo, M. B. Yu, K. Chew, J. Ahn, Q. Zhang, T. Osipowicz, and F. Watt, "Effect of radio-frequency bias voltage on the optical and structural properties of hydrogenated amorphous silicon carbide," *Journal of Applied Physics*, vol. 89, pp. 6153-8, 2001.
- [27] M. G. Park, W. S. Choi, B. Hong, Y. T. Kim, and D. H. Yoon, "Dependence of electrical and optical properties of amorphous SiC:H thin films grown by rf plasma enhanced chemical vapor deposition on annealing temperature," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 20, pp. 861-864, 2002.
- [28] D. N. Wright, E. S. Marstein, A. Rognmo, and A. Holt, "Plasma-enhanced chemical vapour-deposited silicon nitride films; The effect of annealing on optical properties and etch rates," *Solar Energy Materials and Solar Cells*, vol. 92, pp. 1091-1098, 2008.
- [29] N. Kashio, H. Kato, Y. Ohki, K. S. Seol, and T. Noma, "Photoluminescence properties of hydrogenated amorphous silicon nitride," Himeji, Japan, 2001, pp. 79-82.
- [30] Z. H. Cen, T. P. Chen, L. Ding, J. D. Ye, Y. Liu, M. Yang, J. I. Wong, Z. Liu, and S. Fung, "Optical Transmission and Photoluminescence of Silicon Nitride Thin Films Implanted with Si Ions," *Electrochemical and Solid-State Letters*, vol. 12, pp. H38-H40, 2009.

- [31]S. V. Deshpande, E. Gulari, S. W. Brown, and S. C. Rand, "Optical properties of silicon nitride films deposited by hot filament chemical vapor deposition," *Journal of Applied Physics*, vol. 77, pp. 6534-41, 1995.
- [32]F. Giorgis, C. Vinegoni, and L. Pavesi, "Optical absorption and photoluminescence properties of a-Si_{1-x}N_x:H films deposited by plasma-enhanced CVD," *Physical Review B (Condensed Matter)*, vol. 61, pp. 4693-8, 2000.
- [33]F. Giorgis, P. Mandracci, L. Dal Negro, C. Mazzoleni, and L. Pavesi, "Optical absorption and luminescence properties of wide-band gap amorphous silicon based alloys," Netherlands, 2000, pp. 588-92.
- [34]M. Molinari, H. Rinnert, and M. Vergnat, "Improvement of the photoluminescence properties in a-SiN_x films by introduction of hydrogen," *Applied Physics Letters*, vol. 79, pp. 2172-4, 2001.
- [35]M. Molinari, H. Rinnert, and M. Vergnat, "Evolution with the annealing treatments of the photoluminescence mechanisms in a-SiN_x:H alloys prepared by reactive evaporation," *Journal of Applied Physics*, vol. 101, pp. 123532-10, 2007.
- [36]R. A. Street, "Luminescence and recombination in hydrogenated amorphous silicon," *Advances in Physics*, vol. 30, pp. 593 - 676, 1981.
- [37]R. A. Street, "Luminescence in amorphous semiconductors," *Advances in Physics*, vol. 25, pp. 397 - 453, 1976.
- [38]J. I. Pankove, "Radiative recombination in hydrogenated amorphous silicon," *Czechoslovak Journal of Physics*, vol. 30, pp. 355-364, 1980.

- [39]J. I. Pankove and D. E. Carlson, "Electroluminescence in amorphous silicon," *Applied Physics Letters*, vol. 29, pp. 620-622, 1976.
- [40]D. A. Anderson and W. E. Spear, "Electrical and optical properties of amorphous silicon carbide, silicon nitride and germanium carbide prepared by the glow discharge technique," *Philosophical Magazine*, vol. 35, pp. 1-16, 1977.
- [41]L. Kamyab, Rusli., M. B. Yu, L. He, and M. Dua, "Investigation of Optical Properties and Photoluminescence of Amorphous Silicon Carbide in a-SiC/Si₃N₄ Quantum Well Structures Fabricated by PECVD Technique," *ECS Transactions - Vienna, Austria*, vol. 25, 2009.
- [42]D. Kruangam, M. Deguchi, Y. Hattori, T. Toyama, H. Okamoto, and O. Hamakawa, "Amorphous silicon-carbide multilayered visible-light emitting diode," Pittsburgh, PA, USA, 1987, pp. 609-14.
- [43]T. Ma, J. Xu, K. Chen, J. Du, W. Li, and X. Huang, "Red--green--blue light emission from hydrogenated amorphous silicon carbide films prepared by using organic compound xylene as carbon source," *Applied Physics Letters*, vol. 72, pp. 13-15, 1998.
- [44]S. M. Paasche, T. Toyama, H. Okamoto, and Y. Hamakawa, "Amorphous-SiC thin-film p-i-n light-emitting diode using amorphous-SiN hot-carrier tunneling injection layers," *IEEE Transactions on Electron Devices*, vol. 36, pp. 2895-902, 1989.
- [45]T. Rajagopalan, X. Wang, B. Lahlouh, C. Ramkumar, P. Dutta, and S. Gangopadhyay, "Low temperature deposition of nanocrystalline silicon

- carbide films by plasma enhanced chemical vapor deposition and their structural and optical characterization," *Journal of Applied Physics*, vol. 94, pp. 5252-5260, 2003.
- [46] V. A. Vassilyev, A. S. Volkov, E. Musabekov, E. I. Terukov, S. V. Chernyshov, and Y. M. Shernyakov, "Photoluminescence of amorphous hydrogenated silicon-carbon (a-SiC:H) films," *Journal of Non-Crystalline Solids*, vol. 114, pp. 507-509, 1989.
- [47] A. Walkiewicz-Pietrzykowska, A. M. Wrobel, and B. Glebocki, "Properties of Amorphous Hydrogenated Silicon Carbide (a-SiC:H) Films Formed by Remote Hydrogen Microwave Plasma CVD From a Triethylsilane Precursor: Part 2," *Chemical Vapor Deposition*, vol. 15, pp. 47-52, 2009.
- [48] M. B. Yu, Rusli, S. F. Yoon, Z. M. Chen, J. Ahn, Q. Zhang, K. Chew, and J. Cui, "Deposition of nanocrystalline cubic silicon carbide films using the hot-filament chemical-vapor-deposition method," *Journal of Applied Physics*, vol. 87, pp. 8155-8158, 2000.
- [49] C. Song, R. Huang, X. Wang, Y. Guo, J. Song, Y. Zhang, and Z. Zheng, "Effects of hydrogen on photoluminescence properties of a-SiN_x:H films prepared by VHF-PECVD," *Applied Surface Science*, vol. 258, pp. 1290-1293, 2011.
- [50] B. H. Kim, R. F. Davis, and S.-J. Park, "Optical property of silicon quantum dots embedded in silicon nitride by thermal annealing," *Thin Solid Films*, vol. 518, pp. 1744-1746, 2010.

- [51] L. D. Negro, J. H. Yi, J. Michel, L. C. Kimerling, T. W. F. Chang, V. Sukhovatkin, and E. H. Sargent, "Light emission efficiency and dynamics in silicon-rich silicon nitride films," *Applied Physics Letters*, vol. 88, pp. 233109-3, 2006.
- [52] M. Wang, D. Li, Z. Yuan, D. Yang, and D. Que, "Photoluminescence of Si-rich silicon nitride: Defect-related states and silicon nanoclusters," *Applied Physics Letters*, vol. 90, pp. 131903-3, 2007.
- [53] Z. H. Cen, T. P. Chen, L. Ding, Y. Liu, J. I. Wong, M. Yang, Z. Liu, W. P. Goh, F. R. Zhu, and S. Fung, "Strong violet and green-yellow electroluminescence from silicon nitride thin films multiply implanted with Si ions," *Applied Physics Letters*, vol. 94, pp. 041102-3, 2009.
- [54] N.-M. Park, C.-J. Choi, T.-Y. Seong, and S.-J. Park, "Quantum Confinement in Amorphous Silicon Quantum Dots Embedded in Silicon Nitride," *Physical Review Letters*, vol. 86, p. 1355, 2001.
- [55] A. V. Vishnyakov, Y. N. Novikov, V. A. Gritsenko, and K. A. Nasyrov, "The charge transport mechanism in silicon nitride: Multi-phonon trap ionization," *Solid-State Electronics*, vol. 53, pp. 251-255, 2009.
- [56] C. Ricciardi, V. Ballarini, M. Galli, M. Liscidini, L. C. Andreani, M. Losurdo, G. Bruno, S. Lettieri, F. Gesuele, P. Maddalena, and F. Giorgis, "Amorphous Silicon Nitride: a suitable alloy for optical multilayered structures," *Journal of Non-Crystalline Solids*, vol. 352, pp. 1294-1297, 2006.

- [57]Y. Liu, Y. Zhou, W. Shi, L. Zhao, B. Sun, and T. Ye, "Study of photoluminescence spectra of Si-rich SiN_x films," *Materials Letters*, vol. 58, pp. 2397-2400, 2004.
- [58]M. Gupta, V. K. Rathi, R. Thangaraj, O. P. Agnihotri, and K. S. Chari, "The preparation, properties and applications of silicon nitride thin films deposited by plasma-enhanced chemical vapor deposition," *Thin Solid Films*, vol. 204, pp. 77-106, 1991.
- [59]A. Aydmli, A. Serpenguzel, and D. Vardar, "Visible photoluminescence from low temperature deposited hydrogenated amorphous silicon nitride," *Solid State Communications*, vol. 98, pp. 273-7, 1996.
- [60]L. T. Canham, "Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers," *Applied Physics Letters*, vol. 57, pp. 1046-50, 1990.
- [61]L. T. Canham, "Luminescence Bands and their Proposed Origins In Highly Porous Silicon," *physica status solidi (b)*, vol. 190, pp. 9-14, 1995.
- [62]A. G. Cullis and L. T. Canham, "Visible light emission due to quantum size effects in highly porous crystalline silicon," *Nature*, vol. 353, pp. 335-338, 1991.
- [63]N.-M. Park, T.-S. Kim, and S.-J. Park, "Band gap engineering of amorphous silicon quantum dots for light-emitting diodes," *Applied Physics Letters*, vol. 78, pp. 2575-2577, 2001.
- [64]L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzo, and F. Priolo, "Optical gain in silicon nanocrystals," *Nature*, vol. 408, pp. 440-444, 2000.

- [65]D. J. Lockwood, *Light emission in silicon : from physics to devices*. San Diego: Academic Press, 1998.
- [66]J. Heitmann, F. Müller, M. Zacharias, and U. Gösele, "Silicon Nanocrystals: Size Matters," *Advanced Materials*, vol. 17, pp. 795-803, 2005.
- [67]Y. Kanemitsu and S. Okamoto, "Phonon structures and Stokes shift in resonantly excited luminescence of silicon nanocrystals," *Physical Review B*, vol. 58, pp. 9652-9655, 1998.
- [68]N. Dalbosso, M. Luppi, S. Ossicini, E. Degoli, R. Magri, G. Dalba, P. Fornasini, R. Grisenti, F. Rocca, L. Pavesi, S. Boninelli, F. Priolo, C. Spinella, and F. Iacona, "Role of the interface region on the optoelectronic properties of silicon nanocrystals embedded in SiO₂," *Physical Review B*, vol. 68, p. 085327, 2003.
- [69]M. Maus, G. Ganteför, and W. Eberhardt, "The electronic structure and the band gap of nano-sized Si particles: competition between quantum confinement and surface reconstruction," *Applied Physics A: Materials Science & Processing*, vol. 70, pp. 535-539, 2000.
- [70]L. Jiang, X. Zeng, and X. Zhang, "The effects of annealing temperature on photoluminescence of silicon nanoparticles embedded in SiN_x matrix," *Journal of Non-Crystalline Solids*, vol. 357, pp. 2187-2191, 2011.
- [71]F. F. Ren, M. B. Yu, J. D. Ye, Q. Chen, S. T. Tan, G. Q. Lo, and D. L. Kwong, "Strong vertical light output from thin silicon rich oxide/ Si O₂ multilayers via in-plane modulation of photonic crystal patterns," *Applied Physics Letters*, vol. 93, 2008.

- [72]J. Valenta, N. Lalic, and J. Linnros, "Electroluminescence of single silicon nanocrystals," *Applied Physics Letters*, vol. 84, pp. 1459-1461, 2004.
- [73]G. Franzò, A. Irrera, E. C. Moreira, M. Miritello, F. Iacona, D. Sanfilippo, G. Di Stefano, P. G. Fallica, and F. Priolo, "Electroluminescence of silicon nanocrystals in MOS structures," *Applied Physics A: Materials Science & Processing*, vol. 74, pp. 1-5, 2002.
- [74]P. Photopoulos and A. G. Nassiopoulou, "Room- and low-temperature voltage tunable electroluminescence from a single layer of silicon quantum dots in between two thin SiO₂ layers," *Applied Physics Letters*, vol. 77, pp. 1816-1818, 2000.
- [75]M. Wang, A. Anopchenko, A. Marconi, E. Moser, S. Prezioso, L. Pavesi, G. Pucker, P. Bellutti, and L. Vanzetti, "Light emitting devices based on nanocrystalline-silicon multilayer structure," *Physica E: Low-dimensional Systems and Nanostructures*, vol. 41, pp. 912-915, 2009.
- [76]W. K. Tan, M. B. Yu, Q. Chen, J. D. Ye, G. Q. Lo, and D. L. Kwong, "Red light emission from controlled multilayer stack comprising of thin amorphous silicon and silicon nitride layers," *Applied Physics Letters*, vol. 90, 2007.
- [77]W. K. Tan, M. B. Yu, Q. Chen, J. D. Ye, G. Q. Lo, and D. L. Kvvong, "Visible luminescence from controlled multi-layer stack comprising of thin amorphous silicon and silicon nitride layers," Piscataway, NJ, USA, 2007, pp. 88-90.
- [78]H. Rui, D. Hengping, W. Danqing, C. Kunji, D. Honglin, W. Xiang, L. Wei, X. Jun, and M. Zhongyuan, "Role of barrier layers in electroluminescence from

- SiN-based multilayer light-emitting devices," *Applied Physics Letters*, vol. 92, pp. 181106-1, 2008.
- [79] D. Hengping, W. Danqing, C. Kunji, H. Jian, S. Hongcheng, L. Wei, X. Jun, and M. Zhongyuan, "Field dependent electroluminescence from amorphous Si/SiNx multilayer structure," *Applied Physics Letters*, vol. 94, p. 161101 (3 pp.), 2009.
- [80] F. Giorgis, C. F. Pirri, C. Vinegoni, and L. Pavesi, "Luminescence processes in amorphous hydrogenated silicon-nitride nanometric multilayers," *Physical Review B*, vol. 60, p. 11572, 1999.
- [81] Z. H. Lu, D. J. Lockwood, and J. M. Baribeau, "Quantum confinement and light emission in SiO₂/Si superlattices," *Nature*, vol. 378, pp. 258-260, 1995.
- [82] D. J. Lockwood, Z. H. Lu, and J. M. Baribeau, "Quantum Confined Luminescence in Si/SiO₂ Superlattices," *Physical Review Letters*, vol. 76, p. 539, 1996.
- [83] L. Ding, M. B. Yu, X. Tu, G. Q. Lo, S. Tripathy, and T. P. Chen, "Laterally-current-injected light-emitting diodes based on nanocrystalline-Si/SiO₂ superlattice," *Opt. Express*, vol. 19, pp. 2729-2738, 2011.
- [84] L. Kamyab, Rusli, M. B. Yu, L. Ding, and G. Q. Lo, "Electroluminescence from amorphous-SiN_x:H/SiO₂ multilayers using lateral carrier injection," *Applied Physics Letters*, vol. 98, pp. 061105-3, 2011.
- [85] W. K. Tan, Q. Chen, J. D. Ye, M. B. Yu, L. Guo-Qiang, and D. L. Kwong, "Dual-color electroluminescence (450 nm and 650-700 nm) from a silicon-based light source," *IEEE Electron Device Letters*, vol. 29, pp. 344-6, 2008.

- [86]W. K. Tan, M. B. Yu, Q. Chen, W. Y. Loh, J. D. Ye, X. H. Zhang, G. Q. Lo, and D. L. Kwong, "Thin amorphous Si/Si₃N₄-based light-emitting device prepared with low thermal budget," *IEEE Electron Device Letters*, vol. 29, pp. 228-31, 2008.
- [87]L. Kamyab, Rusli., M. B. Yu, L. He, and M. Dua, "Optical Properties and Visible Room Temperature Photoluminescence of Amorphous Silicon Rich Silicon Nitride in SiO₂/SiN_x Quantum Well Structures," *International Journal of Nanoscience*, 2009.
- [88]M. Serenyi, T. Lohner, P. Petrik, and C. Frigeri, "Comparative analysis of amorphous silicon and silicon nitride multilayer by spectroscopic ellipsometry and transmission electron microscopy," *Thin Solid Films*, vol. 515, pp. 3559-62, 2007.
- [89]R. A. Street, *Hydrogenated amorphous silicon*. Cambridge ; New York: Cambridge University Press, 1991.
- [90]J. Dong and D. A. Drabold, "Atomistic Structure of Band-Tail States in Amorphous Silicon," *Physical Review Letters*, vol. 80, pp. 1928-1931, 1998.
- [91]G. D. Cody, T. Tiedje, B. Abeles, B. Brooks, and Y. Goldstein, "Disorder and the Optical-Absorption Edge of Hydrogenated Amorphous Silicon," *Physical Review Letters*, vol. 47, pp. 1480-1483, 1981.
- [92]M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, "Simple Band Model for Amorphous Semiconducting Alloys," *Physical Review Letters*, vol. 22, pp. 1065-1068, 1969.

- [93]D. J. Dunstan and F. Boulitrop, "Photoluminescence in hydrogenated amorphous silicon," *Physical Review B (Condensed Matter)*, vol. 30, pp. 5945-57, 1984.
- [94]S. O. Kasap and P. Capper, *Springer handbook of electronic and photonic materials*. New York: Springer, 2006.
- [95]Y. Tawada, M. Kondo, H. Okamoto, and Y. Hamakawa, "a-SiC:H/a-Si:H heterojunction solar cell having more than 7.5% conversion efficiency," New York, NY, USA, 1981, pp. 245-6.
- [96]D. Pysch, J. Ziegler, J. P. Becker, D. Suwito, S. Janz, S. W. Glunz, and M. Hermie, "Potentials and development of amorphous silicon carbide heterojunction solar cells," Philadelphia, PA, United states, 2009, pp. 000794-000799.
- [97]Y. Tawada, M. Kondo, H. Okamoto, and Y. Hamakawa, "Hydrogenated amorphous silicon carbide as a window material for high efficiency a-Si solar cells," *Solar Energy Materials*, vol. 6, pp. 299-315, 1982.
- [98]I. A. Yunaz, K. Hashizume, S. Miyajima, A. Yamada, and M. Konagai, "Fabrication of amorphous silicon carbide films using VHF-PECVD for triple-junction thin-film solar cell applications," *Solar Energy Materials and Solar Cells*, vol. 93, pp. 1056-1061, 2009.
- [99]H. Munekata, S. Murasato, and H. Kukimoto, "White photoluminescence of amorphous silicon-carbon alloy prepared by glow-discharge decomposition of tetramethylsilane," *Applied Physics Letters*, vol. 37, pp. 536-537, 1980.

- [100] J. Niemann and W. Bauhofer, "Properties of $a\text{-Si}_{1-x}\text{C}_x\text{H}$ thin films deposited from the organosilane Triethylsilane," *Thin Solid Films*, vol. 352, pp. 249-258, 1999.
- [101] S. J. Xu, M. B. Yu, Rusli, S. F. Yoon, and C. M. Che, "Time-resolved photoluminescence spectra of strong visible light-emitting SiC nanocrystalline films on Si deposited by electron-cyclotron-resonance chemical-vapor deposition," *Applied Physics Letters*, vol. 76, pp. 2550-2552, 2000.
- [102] Rusli, S. R. P. Silva, and G. A. J. Amaratunga, "The optical properties of band-gap-modulated diamond-like carbon thin films," *Diamond and Related Materials*, vol. 3, pp. 817-820, 1994.
- [103] F. Demichelis, C. F. Pirri, E. Tresso, H. Herremans, W. Grevendonk, G. J. Adriaenssens, G. Amato, and U. Coscia, "Investigation on electronic density of states in $a\text{-Si}_{1-x}\text{C}_x\text{H}$ films," *Applied Surface Science*, vol. 70-71, pp. 664-668, 1993.
- [104] J. D. Oberstar and B. G. Streetman, "Thin film encapsulants for annealing GaAs and InP," *Thin Solid Films*, vol. 103, pp. 17-26, 1983.
- [105] M. D. Dange, J. Y. Lee, and K. Sooriakumar, "New applications of low temperature PECVD silicon nitride films for microelectronic device fabrication," *Microelectronics Journal*, vol. 22, pp. 19-26, 1991.
- [106] T. P. Ma, "Making silicon nitride film a viable gate dielectric," *IEEE Transactions on Electron Devices*, vol. 45, pp. 680-90, 1998.
- [107] K. G. D. Randhir P S Thakur, Zhiqiang Wu, Alan R Reinberg, "Method and apparatus for reducing isolation stress in integrated circuits

" 6051511, 2002

- [108] M. A. U. Todd, "CVD synthesis of silicon nitride materials," 2005.
- [109] K. Ikeda, R. Saperstein, N. Alic, and Y. Fainman, "Nonlinear optics in silicon nitride waveguide device on silicon chip," Piscataway, NJ, USA, 2008, p. 2 pp.
- [110] M. W. McCutcheon and M. Loncar, "Design of a silicon nitride photonic crystal nanocavity with a Quality factor of one million for coupling to a diamond nanocrystal," *Opt. Express*, vol. 16, pp. 19136-19145, 2008.
- [111] J. Yoo, J. So, G. Yu, and J. Yi, "Study on hydrogenated silicon nitride for application of high efficiency crystalline silicon solar cells," *Solar Energy Materials and Solar Cells*, vol. 95, pp. 7-10, 2010.
- [112] S. M. Sze, *Physics of semiconductor devices*. New York,: Wiley-Interscience, 1969.
- [113] R. M. Mehra, S. C. Agarwal, S. Rani, R. Shyam, and P. C. Mathur, "Conduction mechanism in amorphous Si films," *Journal of Non-Crystalline Solids*, vol. 43, pp. 345-351, 1981.
- [114] P. A. Walley, "Electrical conduction in amorphous silicon and germanium," *Thin Solid Films*, vol. 2, pp. 327-336, 1968.
- [115] A. K. Jonscher and P. A. Walley, "Electrical conduction in non-metallic amorphous films," in *Proceedings of the international conference on thin films*, 28 April-2 May 1969, USA, 1969, pp. 662-9.

- [116] Q. Gu, E. A. Schiff, J. B. Chevrier, and B. Equer, "Fundamental transport mechanisms and high field mobility measurements in amorphous silicon," *Journal of Non-Crystalline Solids*, vol. 198-200, pp. 194-197, 1996.
- [117] T. Tiedje, C. R. Wronski, B. Abeles, and J. M. Cebulka, "Electron transport in hydrogenated amorphous silicon: drift mobility and junction capacitance," *Solar Cells*, vol. 2, pp. 301-18, 1980.
- [118] S. Yokoyama, N. Kajihara, M. Hirose, Y. Osaka, T. Yoshihara, and H. Abe, "Characterization of plasma-deposited silicon nitride films," *Journal of Applied Physics*, vol. 51, pp. 5470-5474, 1980.
- [119] K. D. Vargheese and G. M. Rao, "Electrical properties of silicon nitride films prepared by electron cyclotron resonance assisted sputter deposition," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 19, pp. 2122-2126, 2001.
- [120] J. G. Simmons, "Poole-Frenkel Effect and Schottky Effect in Metal-Insulator-Metal Systems," *Physical Review*, vol. 155, pp. 657-660, 1967.
- [121] L. Fritzsche and W. Bobe, "Poole-Frenkel conduction mechanism in amorphous GeSe films," *Physica Status Solidi B*, vol. 58, pp. 49-52, 1973.
- [122] R. M. Hill, "Poole-Frenkel conduction in amorphous solids," *Philosophical Magazine*, vol. 23, pp. 59-86, 1971.
- [123] W. K. Choi, L. J. Han, and F. L. Loo, "Electrical characterization of radio frequency sputtered hydrogenated amorphous silicon carbide films," *Journal of Applied Physics*, vol. 81, pp. 276-80, 1997.

- [124] J. Yoo-Chan, L. Ho-Young, and J. Seung-Ki, "Electrical properties of silicon nitride thin films fabricated by ECR PECVD at room temperature," in *Amorphous Insulating Thin Films Symposium, 1-4 Dec. 1992*, Pittsburgh, PA, USA, 1993, pp. 9-14.
- [125] M. Tao, D. Park, S. N. Mohammad, D. Li, A. E. Botchkerav, and H. Morkoç, "Electrical conduction in silicon nitrides deposited by plasma enhanced chemical vapour deposition," *Philosophical Magazine Part B*, vol. 73, pp. 723-736, 1996/04/01 1996.
- [126] J. Zhou, G. R. Chen, Y. Liu, J. Xu, T. Wang, N. Wan, Z. Y. Ma, W. Li, C. Song, and K. J. Chen, "Electroluminescent devices based on amorphous SiN/Si quantum dots/amorphous SiN sandwiched structures," *Optics Express*, vol. 17, pp. 156-162, 2009.
- [127] J. Wang, L. Wu, K. Chen, L. Yu, X. Wang, J. Song, and X. Huang, "Charge storage in self-aligned doubly stacked Si nanocrystals in Si Nx dielectric," *Journal of Applied Physics*, vol. 101, 2007.
- [128] L. T. Canham, T. I. Cox, A. Loni, and A. J. Simons, "Progress towards silicon optoelectronics using porous silicon technology," *Applied Surface Science*, vol. 102, pp. 436-441, 1996.
- [129] A. G. Cullis, L. T. Canham, and P. D. J. Calcott, "The structural and luminescence properties of porous silicon," *Journal of Applied Physics*, vol. 82, pp. 909-965, 1997.
- [130] M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, "Modification of visible light emission from silicon nanocrystals as a function

- of size, electronic structure, and surface passivation," Warrendale, PA, USA, 1999, pp. 185-90.
- [131] M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, "Electronic States and Luminescence in Porous Silicon Quantum Dots: The Role of Oxygen," *Physical Review Letters*, vol. 82, p. 197, 1999.
- [132] G. Ledoux, O. Guillois, D. Porterat, C. Reynaud, F. Huisken, B. Kohn, and V. Paillard, "Photoluminescence properties of silicon nanocrystals as a function of their size," *Physical Review B*, vol. 62, pp. 15942-15951, 2000.
- [133] L. Dal Negro, L. Pavesi, G. Pucker, G. Franz², and F. Priolo, "Optical gain in silicon nanocrystals," *Optical Materials*, vol. 17, pp. 41-44, 2001/7// 2001.
- [134] G. Franzo, F. Lacona, C. Spinella, S. Cammarata, and M. G. Grimaldi, "Size dependence of the luminescence properties in Si nanocrystals," *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, vol. 69, pp. 454-458, 2000.
- [135] Y. Kanemitsu, "Efficient light emission from crystalline and amorphous silicon nanostructures," *Journal of Luminescence*, vol. 100, pp. 209-217, 2002.
- [136] Y. Kanemitsu, Y. Fukunishi, and T. Kushida, "Decay dynamics of visible luminescence in amorphous silicon nanoparticles," *Applied Physics Letters*, vol. 77, pp. 211-213, 2000.
- [137] P. Photopoulos, A. G. Nassiopoulou, D. N. Kouvatsos, and A. Travlos, "Photo- and electroluminescence from nanocrystalline silicon single and

- multilayer structures," *Materials Science and Engineering: B*, vol. 69, pp. 345-349, 2000.
- [138] H. Rinnert, M. Vergnat, and A. Burneau, "Evidence of light-emitting amorphous silicon clusters confined in a silicon oxide matrix," *Journal of Applied Physics*, vol. 89, pp. 237-243, 2001.
- [139] S.-I. Tsutomu, E. H. David, and W. B. Ian, "Mechanism of photoluminescence of Si nanocrystals in SiO₂ fabricated by ion implantation: the role of interactions of nanocrystals and oxygen," *Journal of Physics: Condensed Matter*, vol. 11, p. 6595, 1999.
- [140] R. J. Walters, G. I. Bourianoff, and H. A. Atwater, "Field-effect electroluminescence in silicon nanocrystals," *Nat Mater*, vol. 4, pp. 143-146, 2005.
- [141] W. L. Wilson, P. F. Szajowski, and L. E. Brus, "Quantum confinement in size-selected, surface-oxidized silicon nanocrystals," *Science*, vol. 262, pp. 1242-1244, 1993.
- [142] R. K. Soni, L. F. Fonseca, O. Resto, M. Buzaianu, and S. Z. Weisz, "Size-dependent optical properties of silicon nanocrystals," *Journal of Luminescence*, vol. 83, pp. 187-191, 1999.
- [143] L. Pavesi and D. J. Lockwood, *Silicon photonics*. Berlin ; New York: Springer, 2004.
- [144] Y. Kanzawa, T. Kageyama, S. Takeoka, M. Fujii, S. Hayashi, and K. Yamamoto, "Size-dependent near-infrared photoluminescence spectra of Si

- nanocrystals embedded in SiO₂ matrices," *Solid State Communications*, vol. 102, pp. 533-7, 1997.
- [145] P. Mutti, G. Ghislotti, S. Bertoni, L. Bonoldi, G. F. Cerofolini, L. Meda, E. Grilli, and M. Guzzi, "Room-temperature visible luminescence from silicon nanocrystals in silicon implanted SiO₂ layers," *Applied Physics Letters*, vol. 66, pp. 851-853, 1995.
- [146] K.-M. Lee, T.-H. Kim, J.-D. Hwang, S. Jang, K. Jeong, M. Han, S. Won, J. Sok, K. Park, and W.-S. Hong, "Size control of silicon nanocrystals in silicon nitride film deposited by catalytic chemical vapor deposition at a low temperature (≤ 200 C)," *Scripta Materialia*, vol. 60, pp. 703-705, 2009.
- [147] H. Wong and C. K. Wong, "Growth of dielectric-embedded silicon nanocrystallites for silicon integrated photonics," Nis, Serbia, 2010, pp. 15-19.
- [148] F. Iacona, G. Franzo, and C. Spinella, "Correlation between luminescence and structural properties of Si nanocrystals," *Journal of Applied Physics*, vol. 87, pp. 1295-1303, 2000.
- [149] M. Carrada, A. Zerga, M. Amann, J. J. Grob, J. P. Stoquert, A. Slaoui, C. Bonafos, and S. Schamm, "Structural and optical properties of high density Si-nanocrystals synthesized in SiN_x:H by remote PECVD and annealing," *Materials Science and Engineering: B*, vol. 147, pp. 218-221, 2008.
- [150] T.-W. Kim, C.-H. Cho, B.-H. Kim, and S.-J. Park, "Quantum confinement effect in crystalline silicon quantum dots in silicon nitride grown using SiH₄ and NH₃," *Applied Physics Letters*, vol. 88, pp. 123102-3, 2006.

- [151] M. Zhu, Y. Han, R. B. Wehrspohn, C. Godet, R. Etemadi, and D. Ballutaud, "The origin of visible photoluminescence from silicon oxide thin films prepared by dual-plasma chemical vapor deposition," *Journal of Applied Physics*, vol. 83, pp. 5386-5393, 1998.
- [152] K. Ma, J. Y. Feng, and Z. J. Zhang, "Improved photoluminescence of silicon nanocrystals in silicon nitride prepared by ammonia sputtering," *Nanotechnology*, vol. 17, pp. 4650-4653, 2006.
- [153] R. Huang, J. Song, X. Wang, Y. Q. Guo, C. Song, Z. H. Zheng, X. L. Wu, and P. K. Chu, "Origin of strong white electroluminescence from dense Si nanodots embedded in silicon nitride," *Optics Letters*, vol. 37, pp. 692-694.
- [154] M. Molinari, H. Rinnert, M. Vergnat, and P. Weisbecker, "Evolution with annealing treatments of the size of silicon nanocrystallites embedded in a SiN_x matrix and correlation with optical properties," *Materials Science and Engineering B*, vol. 101, pp. 186-189, 2003.
- [155] Y. Q. Wang, Y. G. Wang, L. Cao, and Z. X. Cao, "High-efficiency visible photoluminescence from amorphous silicon nanoparticles embedded in silicon nitride," *Applied Physics Letters*, vol. 83, pp. 3474-3476, 2003.
- [156] B. Rezgui, A. Sibai, T. Nychyporuk, M. Lemiti, and G. Brémond, "Photoluminescence and optical absorption properties of silicon quantum dots embedded in Si-rich silicon nitride matrices," *Journal of Luminescence*, vol. In Press, Corrected Proof, 2009.

- [157] C. K. Wong, V. Filip, H. Wong, S. Stefan, and M. Chan, "Preparation of si nanocrystallites by phase separation of si-rich silicon nitride," Nis, Rs, 2008, pp. 99-102.
- [158] V. A. Gritsenko, K. S. Zhuravlev, A. D. Milov, H. Wong, R. W. M. Kwok, and J. B. Xu, "Silicon dots/clusters in silicon nitride: photoluminescence and electron spin resonance," *Thin Solid Films*, vol. 353, pp. 20-24, 1999.
- [159] Y. Wang, D. Shen, Y. Liu, J. Zhang, Z. Zhang, Y. Liu, Y. Lu, and X. Fan, "Visible photoluminescence of Si clusters embedded in silicon nitride films by plasma-enhanced chemical vapor deposition," *Physica E: Low-dimensional Systems and Nanostructures*, vol. 27, pp. 284-289, 2005.
- [160] B.-H. Kim, C.-H. Cho, T.-W. Kim, N.-M. Park, G. Y. Sung, and S.-J. Park, "Photoluminescence of silicon quantum dots in silicon nitride grown by NH₃ and SiH₄," *Applied Physics Letters*, vol. 86, pp. 091908-3, 2005.
- [161] H. L. Hao, L. K. Wu, W. Z. Shen, and H. F. W. Dekkers, "Origin of visible luminescence in hydrogenated amorphous silicon nitride," *Applied Physics Letters*, vol. 91, pp. 201922-1, 2007.
- [162] B. M. Monroy, O. Cregut, M. Gallart, B. Honerlage, and P. Gilliot, "Optical gain observation on silicon nanocrystals embedded in silicon nitride under femtosecond pumping," *Applied Physics Letters*, vol. 98, 2011.
- [163] W. Ding, L. Zhen, J. Zhang, Y. Li, W. Yu, and G. Fu, "Effect of hydrogen dilution on growth of silicon nanocrystals embedded in silicon nitride thin film

- by plasma-enhanced CVD," *Plasma Science and Technology*, vol. 9, pp. 599-602, 2007.
- [164] L. Tsybeskov and D. J. Lockwood, "Silicon-germanium nanostructures for light emitters and on-chip optical interconnects," *Proceedings of the IEEE*, vol. 97, pp. 1284-1303, 2009.
- [165] L. C. Lenchyshyn, M. L. W. Thewalt, J. C. Sturm, P. V. Schwartz, E. J. Prinz, N. L. Rowell, J. P. Noel, and D. C. Houghton, "High quantum efficiency photoluminescence from localized excitons in $\text{Si}_{1-x}\text{Ge}_x$," *Applied Physics Letters*, vol. 60, pp. 3174-3176, 1992.
- [166] J. Weber and M. I. Alonso, "Near-band-gap photoluminescence of Si-Ge alloys," *Physical Review B*, vol. 40, pp. 5683-5693, 1989.
- [167] J. C. Sturm, H. Manoharan, L. C. Lenchyshyn, M. L. W. Thewalt, N. L. Rowell, J. P. Noel, and D. C. Houghton, "Well-resolved band-edge photoluminescence of excitons confined in strained $\text{Si}_{1-x}\text{Ge}_x$ quantum wells," *Physical Review Letters*, vol. 66, pp. 1362-5, 1991.
- [168] L. Jonghun, "Light-induced changes in the electrical conductivities and photoluminescence in undoped amorphous germanium and silicon-germanium alloys of small x ," *Journal of the Korean Physical Society*, vol. 28, pp. 594-8, 1995.
- [169] L. Hosun, C. Suk-Ho, and T. Y. Seong, "Origin of dislocation-related photoluminescence bands in very thin silicon-germanium layers grown on silicon substrates," *Applied Physics Letters*, vol. 71, pp. 3823-5, 1997.

- [170] R. Ranganathan, M. Gal, J. M. Viner, and P. C. Taylor, "Photoluminescence in hydrogenated silicon-germanium alloys," in *Amorphous Silicon Semiconductors - Pure and Hydrogenated. Symposium, 21-25 April 1987*, Pittsburgh, PA, USA, 1987, pp. 293-8.
- [171] Y. Shiraki and A. Sakai, "Fabrication technology of SiGe hetero-structures and their properties," *Surface Science Reports*, vol. 59, pp. 153-207, 2005.
- [172] J. M. Baribeau, R. Pascual, and S. Saimoto, "Interdiffusion and strain relaxation in (Si_mGe_n)_p superlattices," *Applied Physics Letters*, vol. 57, pp. 1502-1504, 1990.
- [173] D. J. Robbins, L. T. Canham, S. J. Barnett, A. D. Pitt, and P. Calcott, "Near-band-gap photoluminescence from pseudomorphic Si_{1-x}Ge_x single layers on silicon," *Journal of Applied Physics*, vol. 71, pp. 1407-14, 1992.
- [174] P. Schittenhelm, M. Gail, J. Brunner, J. F. Nutzel, and G. Abstreiter, "Photoluminescence study of the crossover from two-dimensional to three-dimensional growth for Ge on Si(100)," *Applied Physics Letters*, vol. 67, pp. 1292-1294, 1995.
- [175] R. Apetz, L. Vescan, A. Hartmann, C. Dieker, and H. Luth, "Photoluminescence and electroluminescence of SiGe dots fabricated by island growth," *Applied Physics Letters*, vol. 66, pp. 445-7, 1995.
- [176] O. G. Schmidt, C. Lange, and K. Eberl, "Photoluminescence study of the initial stages of island formation for Ge pyramids/domes and hut clusters on Si(001)," *Applied Physics Letters*, vol. 75, pp. 1905-1907, 1999.

- [177] B. V. Kamenev, L. Tsybeskov, J. M. Baribeau, and D. J. Lockwood, "Photoluminescence and Raman scattering in three-dimensional Si/Si_{1-x}Ge_x nanostructures," *Applied Physics Letters*, vol. 84, pp. 1293-1295, 2004.
- [178] M. Forbes, J. Gourlay, and M. Desmulliez, "Optically interconnected electronic chips: A tutorial and review of the technology," *Electronics and Communication Engineering Journal*, vol. 13, pp. 221-223, 2001.
- [179] K. L. Wang and R. P. G. Karunasiri, "SiGe/Si electronics and optoelectronics," in *Topical Conference on Silicon-Based Heterostructures II*, 9-10 Nov. 1992, USA, 1993, pp. 1159-67.
- [180] Z. H. Lu, D. J. Lockwood, and J. M. Baribeau, "Visible light emitting Si/SiO₂ superlattices," *Solid-State Electronics*, vol. 40, pp. 197-201, 1996.
- [181] G. Pucker, P. Bellutti, M. Cazzanelli, Z. Gaburro, and L. Pavesi, "(Si/SiO₂)_n multilayers and microcavities for LED applications," Netherlands, 2001, pp. 27-30.
- [182] M. H. Crawford, "LEDs for solid-state lighting: Performance challenges and recent advances," *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 15, pp. 1028-1040, 2009.
- [183] G. G. Qin, S. Y. Ma, Z. C. Ma, W. H. Zong, and Y. Li-ping, "Electroluminescence from amorphous Si/SiO₂ superlattices," *Solid State Communications*, vol. 106, pp. 329-333, 1998.
- [184] B. Abeles and T. Tiedje, "Amorphous Semiconductor Superlattices," *Physical Review Letters*, vol. 51, p. 2003, 1983.

- [185] S. Kalem, "Optical investigation of a-Si:H/a-SiN_x:H superlattices," *Physical Review B*, vol. 37, p. 8837, 1988.
- [186] K. Murayama, T. Toyama, S. Miyazaki, and M. Hirose, "Fundamental absorption edge spectrum of ultrathin a-Si:H film in a-Si:H/a-Si₃N₄:H multilayer obtained from luminescence excitation spectrum," *Solid State Communications*, vol. 104, pp. 119-23, 1997.
- [187] R. Rizzoli, C. Summonte, P. Rava, G. Barucca, A. Desalvo, and F. Giorgis, "a-SiN:H multilayer versus bulk structure: a real improvement of radiative efficiency?," *Journal of Non-Crystalline Solids*, vol. 266-269, pp. 1062-1066, 2000.
- [188] P. Photopoulos, A. G. Nassiopoulou, D. N. Kouvatsos, and A. Travios, "Photoluminescence from nanocrystalline silicon in Si/SiO₂ superlattices," *Applied Physics Letters*, vol. 76, pp. 3588-90, 2000.
- [189] G. Pucker, P. Bellutti, C. Spinella, K. Gatterer, M. Cazzanelli, and L. Pavesi, "Room temperature luminescence from (Si/SiO₂)_n (n = 1,2,3) multilayers grown in an industrial low-pressure chemical vapor deposition reactor," *Journal of Applied Physics*, vol. 88, pp. 6044-6051, 2000.
- [190] B. Averboukh, R. Huber, K. W. Cheah, Y. R. Shen, G. G. Qin, Z. C. Ma, and W. H. Zong, "Luminescence studies of a Si/SiO₂ superlattice," *Journal of Applied Physics*, vol. 92, pp. 3564-8, 2002.
- [191] J. M. Baribeau, D. J. Lockwood, Z. H. Lu, H. J. Labbé, S. J. Rolfe, and G. I. Sproule, "Amorphous Si/insulator multilayers grown by vacuum deposition

- and electron cyclotron resonance plasma treatment," *Journal of Luminescence*, vol. 80, pp. 417-421, 1998.
- [192] R. Huang, H. Dong, D. Wang, K. Chen, H. Ding, X. Wang, W. Li, J. Xu, and Z. Ma, "Role of barrier layers in electroluminescence from SiN-based multilayer light-emitting devices," *Applied Physics Letters*, vol. 92, pp. 181106-3, 2008.
- [193] H. Fujiwara, *Spectroscopic ellipsometry : principles and applications*. Chichester, England ; Hoboken, NJ: John Wiley & Sons, 2007.
- [194] H. G. Tompkins, E. A. Irene, and Knovel (Firm). (2005). *Handbook of ellipsometry*. Available:
<http://www.knovel.com/knovel2/Toc.jsp?BookID=1175> MIT Access Only
- [195] V. K, "Spectroscopic ellipsometry: a historical overview," *Thin Solid Films*, vol. 313-314, pp. 1-9, 1998.
- [196] M. Losurdo, M. Bergmair, G. Bruno, D. Cattelan, C. Cobet, A. De Martino, K. Fleischer, Z. Dohcevic-Mitrovic, N. Esser, M. Galliet, R. Gajic, D. Hemzal, K. Hingerl, J. Humlicek, R. Ossikovski, Z. V. Popovic, and O. Saxl, "Spectroscopic ellipsometry and polarimetry for materials and systems analysis at the nanometer scale: State-of-the-art, potential, and perspectives," *Journal of Nanoparticle Research*, vol. 11, pp. 1521-1554, 2009.
- [197] J. F. Lelièvre, J. De la Torre, A. Kaminski, G. Bremond, M. Lemiti, R. El Bouayadi, D. Araujo, T. Epicier, R. Monna, M. Pirot, P. J. Ribeyron, and C. Jaussaud, "Correlation of optical and photoluminescence properties in

- amorphous SiN_x:H thin films deposited by PECVD or UVCVD," *Thin Solid Films*, vol. 511-512, pp. 103-107, 2006.
- [198] J. Robertson, "Electronic structure of silicon nitride," *Philosophical Magazine Part B*, vol. 63, pp. 47 - 77, 1991.
- [199] T. M. Searle, W. A. Jackson, and I. G. Austin, "Optical properties of amorphous Si:N:H alloys," Netherlands, 1987, pp. 991-8.
- [200] I. G. Austin, W. A. Jackson, T. M. Searle, and P. K. Bhat, "PHOTOLUMINESCENCE PROPERTIES OF a-SiN_x:H ALLOYS," *Philosophical Magazine B: Physics of Condensed Matter; Electronic, Optical and Magnetic Properties*, vol. 52, pp. 271-288, 1985.
- [201] H. Kurata, M. Hirose, and Y. Osaka, "Wide optical-gap, photoconductive a-SiN_{1-x}:H," *Japanese Journal of Applied Physics*, vol. 20, pp. 811-13, 1981.
- [202] Z. Yin and F. W. Smith, "Optical dielectric function and infrared absorption of hydrogenated amorphous silicon nitride films: experimental results and effective-medium-approximation analysis," *Physical Review B (Condensed Matter)*, vol. 42, pp. 3666-75, 1990.
- [203] B. Grolik and J. Kopp, "Optical Properties of Thin Semiconductor Films," *Condensed Matter Physics*, vol. 46, pp. 1-11, 2003.
- [204] M. Stutzmann, "The defect density in amorphous silicon," *Philosophical Magazine Part B*, vol. 60, pp. 531-546, 2012/03/16 1989.
- [205] R. S. Crandall, "Band-Tail Absorption in Hydrogenated Amorphous Silicon," *Physical Review Letters*, vol. 44, pp. 749-752, 1980.

- [206] J. Tong, "Defects in amorphous semiconductors," PhD, The University of Utah, 2007.
- [207] W. B. Jackson, N. M. Amer, A. C. Boccara, and D. Fournier, "Photothermal deflection spectroscopy and detection," *Appl. Opt.*, vol. 20, pp. 1333-1344, 1981.
- [208] A. R. Forouhi and I. Bloomer, "Optical dispersion relations for amorphous semiconductors and amorphous dielectrics," *Physical Review B (Condensed Matter)*, vol. 34, pp. 7018-26, 1986.
- [209] W. A. McGahan, T. Makovicka, J. Hale, and J. A. Woollam, "Modified Forouhi and Bloomer dispersion model for the optical constants of amorphous hydrogenated carbon thin films," *Thin Solid Films*, vol. 253, pp. 57-61, 1994.
- [210] S. A. Alterovitz, R. M. Sieg, N. S. Shoemaker, and J. J. Pouch, "Optical dispersion relations for 'diamondlike' carbon films," Pittsburgh, PA, USA, 1989, pp. 21-6.
- [211] G. E. Jellison, Jr., "Data analysis for spectroscopic ellipsometry," Switzerland, 1993, pp. 416-22.
- [212] J. G. E. Jellison and F. A. Modine, "Parameterization of the optical functions of amorphous materials in the interband region," *Applied Physics Letters*, vol. 69, pp. 371-373, 1996.
- [213] J. G. E. Jellison, F. A. Modine, P. Doshi, and A. Rohatgi, "Spectroscopic ellipsometry characterization of thin-film silicon nitride," *Thin Solid Films*, vol. 313-314, pp. 193-197, 1998.

- [214] Z. H. Cen, T. P. Chen, L. Ding, Y. Liu, M. Yang, J. I. Wong, Z. Liu, Y. C. Liu, and S. Fung, "Annealing effect on the optical properties of implanted silicon in a silicon nitride matrix," *Applied Physics Letters*, vol. 93, pp. 023122-3, 2008.
- [215] J. M. Khoshman and M. E. Kordesch, "Optical absorption in amorphous InN thin films," *Journal of Non-Crystalline Solids*, vol. 352, pp. 5572-5577, 2006.
- [216] V. E. Vamvakas, N. Vourdas, and S. Gardelis, "Optical characterization of Si-rich silicon nitride films prepared by low pressure chemical vapor deposition," *Microelectronics Reliability*, vol. 47, pp. 794-797, 2007/5// 2007.
- [217] M. F. Saenger, J. Sun, M. Schädel, J. Hilfiker, M. Schubert, and J. A. Woollam, "Spectroscopic ellipsometry characterization of SiN_x antireflection films on textured multicrystalline and monocrystalline silicon solar cells," *Thin Solid Films*, vol. 518, pp. 1830-1834, 2009.
- [218] A. S. Ferlauto, G. M. Ferreira, J. M. Pearce, C. R. Wronski, R. W. Collins, X. Deng, and G. Ganguly, "Analytical model for the optical functions of amorphous semiconductors from the near-infrared to ultraviolet: Applications in thin film photovoltaics," *Journal of Applied Physics*, vol. 92, pp. 2424-2436, 2002.
- [219] P. Nemec and M. Frumar, "Photoinduced phenomena in As₄Se₃ amorphous thin films prepared by pulsed laser deposition," *Thin Solid Films*, vol. 516, pp. 8377-80, 2008.

- [220] J. Sancho-Parramon, M. Modreanu, S. Bosch, and M. Stchakovsky, "Optical characterization of HfO₂ by spectroscopic ellipsometry: Dispersion models and direct data inversion," *Thin Solid Films*, vol. 516, pp. 7990-7995, 2008.
- [221] J. Price, P. Y. Hung, T. Rhoad, B. Foran, and A. C. Diebold, "Spectroscopic ellipsometry characterization of Hf_xSi_yO_z films using the Cody-Lorentz parameterized model," *Applied Physics Letters*, vol. 85, pp. 1701-1703, 2004.
- [222] M. Foldyna, K. Postava, J. Bouchala, J. Pistora, and T. Yamaguchi, "Model dielectric functional of amorphous materials including Urbach tail," in *Microwave and Optical Technology 2003*, 2004, pp. 301-305.
- [223] J. J. Mei, H. Chen, W. Z. Shen, and H. F. W. Dekkers, "Optical properties and local bonding configurations of hydrogenated amorphous silicon nitride thin films," *Journal of Applied Physics*, vol. 100, p. 073516, 2006.
- [224] H. Geng, *Semiconductor Manufacturing Handbook*: McGraw-Hill, 2005.
- [225] R. Ghodssi and P. Lin, *MEMS Materials and Processes Handbook*: Springer, 2011.
- [226] D. Hoffman, B. Singh, and I. I. I. J. H. Thomas, *Handbook of Vacuum Science and Technology [electronic resource]*: Burlington : Elsevier, 1997., 1997.
- [227] D. M. Mattox, *Handbook of Physical Vapor Deposition (Pvd) Processing*: Elsevier Science, 2010.

- [228] P. Nagels, *Plasma-enhanced chemical vapour deposition of amorphous As_xSe_{100-x} films*
Chemical Vapor Deposition Proceedings of the Fourteenth International Conference and EUROCVD-11, 1997.
- [229] S. M. Rossnagel, J. J. Cuomo, and W. D. Westwood, *Handbook of plasma processing technology : fundamentals, etching, deposition, and surface interactions / edited by Stephen M. Rossnagel, Jerome J. Cuomo, William D. Westwood*: Park Ridge, N.J., U.S.A. : Noyes Publications, c1990., 1990.
- [230] K. rhoff, P. V. Lambeck, and A. Driessen, "Design, Tolerance Analysis, and Fabrication of Silicon Oxynitride Based Planar Optical Waveguides for Communication Devices," *J. Lightwave Technol.*, vol. 17, p. 1401, 1999.
- [231] L. O. Vasquez, *Fuel Cell Research Trends*: Nova Science Publishers, 2008.
- [232] K. Wasa and S. Hayakawa, *Handbook of Sputter Deposition Technology: Principles, Technology, and Applications*: Noyes Publications, 1992.
- [233] "<https://www.mems-exchange.org/MEMS/processes/deposition.html>."
- [234] K. Seshan, *Handbook of Thin Film Deposition*: Elsevier Science, 2012.
- [235] P. Nae-Man, K. Sang Hyeob, and S. Gun Yong, "Amorphous silicon carbon nitride films grown by the pulsed laser deposition of a SiC-Si₃N₄ mixed target," *ETRI Journal*, vol. 26, pp. 257-61, 2004.
- [236] S. Jeong Dae, S. Gun Yong, and K. Kwang Yong, "Target surface modification and particulates on YBa₂Cu₃O_{7-x} thin film by pulsed laser deposition," in *Layered Superconductors: Fabrication, Properties and*

- Applications. Symposium, 27 April-1 May 1992, Pittsburgh, PA, USA, 1992, pp. 329-34.*
- [237] W. A. Lanford and M. J. Rand, "The hydrogen content of plasma-deposited silicon nitride," *Journal of Applied Physics*, vol. 49, pp. 2473-2477, 1978.
- [238] F. Giorgis, C. F. Pirri, and E. Tresso, "Structural properties of a-Si_{1-x}N_x:H films grown by plasma enhanced chemical vapour deposition by SiH₄ + NH₃ + H₂ gas mixtures," *Thin Solid Films*, vol. 307, pp. 298-305, 1997.
- [239] H. Kato, N. Kashio, Y. Ohki, K. S. Seol, and T. Noma, "Band-tail photoluminescence in hydrogenated amorphous silicon oxynitride and silicon nitride films," *Journal of Applied Physics*, vol. 93, pp. 239-244, 2003.
- [240] I. Pereyra and M. I. Alayo, "High quality low temperature DPECVD silicon dioxide," *Journal of Non-Crystalline Solids*, vol. 212, pp. 225-231, 1997.
- [241] Y. T. Kim, S. M. Cho, Y. G. Seo, H. D. Yoon, Y. M. Im, and D. H. Yoon, "Influence of hydrogen on SiO₂ thick film deposited by PECVD and FHD for silica optical waveguide," *Crystal Research and Technology*, vol. 37, pp. 1257-63, 2002.
- [242] D. B. Williams and C. B. Carter, "The Transmission Electron Microscope Transmission Electron Microscopy," ed: Springer US, 2009, pp. 3-22.
- [243] D. B. Williams and C. B. Carter, *Transmission Electron Microscopy [electronic resource] : A Textbook for Materials Science / by David B. Williams, C. Barry Carter*: Boston, MA : Springer US, 2009.
- 2., 2009.

- [244] D. E. Newbury and D. B. Williams, "The electron microscope: the materials characterization tool of the millennium," *Acta Materialia*, vol. 48, pp. 323-346, 2000.
- [245] G. D. Christian and J. E. O'Reilly, *Instrumental analysis*, 2nd ed. Boston: : Allyn and Bacon, 1986.
- [246] D. R. Vij, *Luminescence of solids*. New York: Plenum Press, 1998.
- [247] A. Kitai, *Solid state luminescence : theory, materials, and devices*, 1st ed. London ; New York: Chapman & Hall, 1993.
- [248] D. K. Schroder, *Semiconductor material and device characterization*, 3rd ed. [Piscataway, NJ] Hoboken, N.J.: IEEE Press ; Wiley, 2006.
- [249] S. T. H. Silalahi, "Development of Silicon Nanostructures as Light Emitter and Sensitizer for Erbium Emission," PhD, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, 2009.
- [250] J. Huang, J. Blochwitz-Nimoth, M. Pfeiffer, and K. Leo, "Influence of the thickness and doping of the emission layer on the performance of organic light-emitting diodes with PiN structure," *Journal of Applied Physics*, vol. 93, pp. 838-844, 2003.
- [251] H. Gufeng, S. Oliver, Q. Dashan, Z. Xiang, P. Martin, and L. Karl, "Very high-efficiency and low voltage phosphorescent organic light-emitting diodes based on a p-i-n junction," *Journal of Applied Physics*, vol. 95, pp. 5773-5777, 2004.

- [252] Y. Taniyasu, M. Kasu, and T. Makimoto, "An aluminium nitride light-emitting diode with a wavelength of 210[thinsp]nanometres," *Nature*, vol. 441, pp. 325-328, 2006.
- [253] P. E. Burrows, Z. Shen, V. Bulovic, D. M. McCarty, S. R. Forrest, J. A. Cronin, and M. E. Thompson, "Relationship between electroluminescence and current transport in organic heterojunction light-emitting devices," *Journal of Applied Physics*, vol. 79, pp. 7991-7991, 1996.
- [254] A. Anopchenko, A. Marconi, E. Moser, S. Prezioso, M. Wang, L. Pavesi, G. Pucker, and P. Bellutti, "Low-voltage onset of electroluminescence in nanocrystalline-Si/SiO₂ multilayers," *Journal of Applied Physics*, vol. 106, p. 033104 (8 pp.), 2009.
- [255] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, and P. Yang, "Nanowire dye-sensitized solar cells," *Nature Materials*, vol. 4, pp. 455-459, 2005.
- [256] P. Mehta, N. Healy, N. F. Baril, P. J. A. Sazio, J. V. Badding, and A. C. Peacock, "Nonlinear transmission properties of hydrogenated amorphous silicon core optical fibers," *Opt. Express*, vol. 18, pp. 16826-16831, 2010.
- [257] S. Ali, M. Gharghi, S. Sivoththaman, and K. Zeaiter, "Properties and characterization of low-temperature amorphous PECVD silicon nitride films for solar cell passivation," 2005, pp. 1469-1473.
- [258] C. Boehme and G. Lucovsky, "Origins of silicon solar cell passivation by SiN_x:H anneal," *Journal of Non-Crystalline Solids*, vol. 299â€“302, Part 2, pp. 1157-1161, 2002.
- [259] !!! INVALID CITATION !!!

- [260] "<http://www.jawoollam.com/>."
- [261] "<http://www.docslide.com/spectroscopic-ellipsometry/>."
- [262] M. K. Smit and J. W. Verhoof, "Accuracy analysis in multiple angle of incidence ellipsometry," *Thin Solid Films*, vol. 189, pp. 193-203, 1990.
- [263] E. D. Palik, *Handbook of optical constants of solids*. Orlando: Academic Press, 1985.
- [264] J.A.WoolamCo., "Guide to Using WVASE32."
- [265] J. Warga, R. Li, S. N. Basu, and L. D. Negro, "Electroluminescence from silicon-rich nitride/silicon superlattice structures," *Applied Physics Letters*, vol. 93, pp. 151116-3, 2008.
- [266] H.-P. Dong and et al., "Strong Green Light Emission from Low-Temperature Grown a-SiN_x:H Film after Different Oxidation Routes," *Chinese Physics Letters*, vol. 25, p. 4147, 2008.
- [267] K. Wakita, S. Makimura, and Y. Nakayama, "Effect of annealing on photoluminescence spectra and film structure in a-SiN_x:H," *Japanese Journal of Applied Physics, Part 1 (Regular Papers & Short Notes)*, vol. 34, pp. 1425-30, 1995.
- [268] P. G. Snyder, M. C. Rost, G. H. Bu-Abbud, J. A. Woollam, and S. A. Alterovitz, "Variable angle of incidence spectroscopic ellipsometry: Application to GaAs-Al_xGa_{1-x}As multiple heterostructures," *Journal of Applied Physics*, vol. 60, pp. 3293-302, 1986.
- [269] R. Huang, K. Chen, B. Qian, S. Chen, W. Li, J. Xu, Z. Ma, and X. Huang, "Oxygen induced strong green light emission from low-temperature grown

- amorphous silicon nitride films," *Applied Physics Letters*, vol. 89, pp. 221120-3, 2006.
- [270] Y. Xin, Y. Shi, H. Liu, Z. X. Huang, L. Pu, R. Zhang, and Y. D. Zheng, "Effect of NH₃ flow rate on growth, structure and luminescence of amorphous silicon nitride films by electron cyclotron resonance plasma," *Thin Solid Films*, vol. 516, pp. 1130-1136, 2008.
- [271] L. Cai, A. Rohatgi, D. Yang, and M. A. El-Sayed, "Effects of rapid thermal anneal on refractive index and hydrogen content of plasma-enhanced chemical vapor deposited silicon nitride films," *Journal of Applied Physics*, vol. 80, pp. 5384-5388, 1996.
- [272] C. Snmaud, A. Gheorghiu, L. Amoura, R. Etemadi, H. Shirai, C. Godet, M. Fang, and S. Gujrathi, "Local order and H-bonding in N-rich amorphous silicon nitride," *Journal of Non-Crystalline Solids*, vol. 164-166, pp. 1073-1076, 1993.
- [273] R. A. Street, D. K. Biegelsen, and J. C. Knights, "Defect states in doped and compensated a-Si: H," *Physical Review B*, vol. 24, pp. 969-984, 1981.
- [274] D. Han, M. Yoshida, and K. Morigaki, "Light-induced photoluminescence fatigue in a-Si:H," *Journal of Non-Crystalline Solids*, vol. 97-98, Part 1, pp. 651-654, 1987.
- [275] L. Tsybeskov and P. M. Fauchet, "Correlation between photoluminescence and surface species in porous silicon: Low-temperature annealing," *Applied Physics Letters*, vol. 64, pp. 1983-1985, 1994.

- [276] K. S. Cho, N.-M. Park, T.-Y. Kim, K.-H. Kim, G. Y. Sung, and J. H. Shin, "High efficiency visible electroluminescence from silicon nanocrystals embedded in silicon nitride using a transparent doping layer," *Applied Physics Letters*, vol. 86, pp. 071909-3, 2005.
- [277] S. Fujita and N. Sugiyama, "Visible light-emitting devices with Schottky contacts on an ultrathin amorphous silicon layer containing silicon nanocrystals," *Applied Physics Letters*, vol. 74, pp. 308-310, 1999.
- [278] J. M. Baribeau, D. J. Lockwood, and Z. H. Lu, "Fabrication and structural and optical properties of amorphous Si/SiO₂ superlattices on (100)Si," Pittsburgh, PA, USA, 1995, pp. 259-64.
- [279] N. Bernhard and G. H. Bauer, "Physical properties of a-Si:H based compositional periodic multilayers," *Physical Review B*, vol. 52, pp. 8829-8847, 1995.
- [280] K. Mui and F. W. Smith, "Optical absorption of amorphous-Si:H/amorphous-Si_xN_{1-x}:H multilayers: Effects of interface alloying," *Journal of Applied Physics*, vol. 63, pp. 475-478, 1988.
- [281] S. Shibata, F. Kawase, A. Kitada, T. Kouzaki, and A. Kitamura, "Evaluation of Pre-amorphized Layer Thickness and Interface Quality of High-Dose Shallow Implanted Silicon by Spectroscopic Ellipsometry," *IEEE Transactions on Semiconductor Manufacturing*, vol. 23, pp. 545-52, 2010.
- [282] G. Zhang, M.-B. Yu, C.-H. Tung, and G.-Q. Lo, "Quantum size effects on dielectric constants and optical absorption of ultrathin silicon films," *IEEE Electron Device Letters*, vol. 29, pp. 1302-1305, 2008.

- [283] H. G. Yoo and P. M. Fauchet, "Dielectric constant reduction in silicon nanostructures," *Physical Review B (Condensed Matter and Materials Physics)*, vol. 77, pp. 115355-1, 2008.
- [284] S. A. Koehler, "Search for quantum confinement effects in ultrathin layers of hydrogenated amorphous silicon," *Philosophical Magazine Part B*, vol. 77, pp. 27-48, 2012/03/05 1998.
- [285] K. Sung, P. Yong Min, C. Suk-Ho, K. Kyung Joong, and C. Dong Hoon, "Temperature-dependent carrier recombination processes in nanocrystalline Si/SiO₂ multilayers studied by continuous-wave and time-resolved photoluminescence," *Journal of Physics D (Applied Physics)*, vol. 40, pp. 1339-42, 2007.
- [286] S. Edward H, "Semiconductor lasers for planar integrated optoelectronics," *Solid-State Electronics*, vol. 44, pp. 147-173, 2000.
- [287] C. Kwan Sik, P. Nae-Man, K. Tae-Youb, K. Kyung-Hyun, S. Gun Yong, and H. S. Jung, "High efficiency visible electroluminescence from silicon nanocrystals embedded in silicon nitride using a transparent doping layer," *Applied Physics Letters*, vol. 86, p. 071909, 2005.
- [288] W. C. Wang and H. Fritzsche, "Time resolved photoluminescence in a-Si : H: A comparison between single layers and superlattices," *Journal of Non-Crystalline Solids*, vol. 97-98, Part 2, pp. 919-922, 1987.
- [289] R. W. Collins, M. A. Paesler, and W. Paul, "The temperature dependence of photoluminescence in a-Si: H alloys," *Solid State Communications*, vol. 34, pp. 833-836, 1980.

- [290] S. Nihonyanagi, K. Nishimoto, and Y. Kanemitsu, "Visible photoluminescence and quantum confinement effects in amorphous Si/SiO₂ multilayer structures," *Journal of Non-Crystalline Solids*, vol. 299-302, pp. 1095-1099, 2002.
- [291] M. Boroditsky, T. F. Krauss, R. Coccioli, R. Bhat, and E. Yablonovitch, "Light extraction from optically pumped light-emitting diode by thin-slab photonic crystals," *Applied Physics Letters*, vol. 75, pp. 1036-8, 1999.
- [292] D. H. Long, I. K. Hwang, and S. W. Ryu, "Design optimization of photonic crystal structure for improved light extraction of GaN LED," *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 15, pp. 1257-1263, 2009.
- [293] F. F. Ren, M. B. Yu, J. D. Ye, Q. Chen, S. T. Tan, G. Q. Lo, and D. L. Kwong, "Two-dimensional photonic crystal patterns for vertical light extraction enhancement from ultra-thin amorphous Si/Si₃N₄ multilayer stack," in *2008 IEEE Photonics Global at Singapore, IPGC 2008*, Singapore, 2008.