Development of silicon nanostructures as light emitter and sensitizer for erbium emission

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Development of Silicon Nanostructures as Light Emitter and Sensitizer for Erbium Emission

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

Date

Samson Tua Halomoan Silalahi

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Summary

One of the motivation of Silicon (Si) photonics was to realize optical interconnect to alleviate the bottleneck encountered in the electrical interconnect, especially in high speed application. The key advantages of Si photonics are its excellent optical properties as well as its high yield and low production cost established in microelectronics industry. Accordingly, Si-based material has been intensively developed for different photonics components, such as light guiding, modulation and light detection. However one underlying fact is that Si-based material has not been successfully developed as a light emitter component, which is an integral part of optical integrated circuits. This is due to the indirect band gap property of Si material.

Nanostructured Si, however, exhibits potential luminescence in visible to NIR wavelength and therefore attracted interest for realizing the light emitting component. Some of the advantages of Si-nanostructures based emitting structure are the broadband excitation wavelength (near UV to visible, 300-500 nm), the controllability of emission wavelength by tailoring the average size of Si nanostructures, as well as the sensitizing effect of Si-nanostructures on Erbium (Er)-related emission. However, there are still several challenges as follows. Firstly, a prolonged annealing in the range of 1100°C is normally implemented to form efficiently emitting Si-nanocrystals. Secondly, in general, controlling the Si-nanocrystal size by varying Si concentration is difficult to achieve. Thirdly, there is a need to optimize the energy transfer from Si-nanostructure and Erbium (Er) ions to increase emission intensity of Si-nanostructures sensitized Er system. Lastly, in the case of light emitting device, a more efficient light extraction is necessary. In this work, these challenges were addressed.

The work was divided into four different parts, namely the development of Si-nanostructures for visible light emission using low-thermal budget treatment such as rapid thermal annealing (RTA) process and forming gas (5%H₂:N₂) annealing, size control of the Si-nanostructures by superlattice arrangement and rapid oxidation, the development of Si-nanostructures sensitizer for Er-related emission at optical communication wavelength (1.55 μ m) by RTA

process, and the development of photonic crystal (PC) slab structure based on Si-nanocrystal and Er doped Si-nanostructure for enhancing the light emission in the range of visible and IR wavelengths, respectively.

The Si nanostructures are in general embedded in insulating host material to provide stability. In this work, SiO₂ was chosen to be the host (embedding) material because of its excellent compatibility with standard Si process technology. The deposition technique used in this work was RF magnetron co-sputtering technique due to the possibility of tailoring the Si, O and Er using three independent Si, SiO₂, and Er₂O₃ magnetron targets. In general, Si nanostructures were formed by annealing the excess Si, which was introduced during the deposition process. In this work, the low thermal budget annealing process was used instead of long conventional annealing at 1100°C. More importantly, the superlattice arrangements, i.e. periodically alternating bi-layers of Si-rich oxide/SiO₂ (SRO/SiO₂) and Er:Si-rich oxide/SiO₂ (Er:SRO/SiO₂) superlattice structures were used.

In the first part of work, the Si-rich oxide/silicon dioxide (SRO/SiO₂) superlattice structures were studied, developed and optimized by RF magnetron co-sputtering method and low thermal budget processes, such as rapid thermal annealing (RTA) and excimer laser annealing (ELA) processes in order to achieve a relatively more controlled size distribution of Si nanocrystals, i.e. well controlled photoluminescence (PL) peak wavelength as a function of the thickness of Si-rich oxide (SRO) layer. The rapid thermal annealing (RTA) process at temperatures ranging from 500°C to 1000°C in N₂ for 2 minutes was implemented on the superlattice samples to study the PL spectra. The excitation wavelength used was 325 nm. After RTA process at 1000°C, the Si nanocrystal related PL peak wavelengths of 768, 802, and 815 nm were observed for samples with SRO layer thickness of 3, 4, 5 nm, respectively. The corresponding average sizes of Si nanocrystals are 3.6 nm, 4.6 nm, and 6 nm as derived from Transmission Electron Microscopy (TEM) characterization results. In addition, oxygen deficiency defect related PL bands at 400 and 515 nm were also observed. Due to such short annealing, PL intensity was relatively weaker than that of samples annealed in longer conventional annealing. By annealing in forming gas (5%H₂:N₂) at temperature of 500°C for 30 minutes to 2 hours, the PL intensity was increased by a factor of ~8 without any observable peak-shift and more importantly the PL intensity is higher than the sample treated by long annealing at 1100°C for 4 hours. This indicates that reduction of defects on the

interface or vicinity of Si-nanocrystals/nanoclusters plays a crucial factor for light emission efficiency of Si-nanocrystals. For comparison, the Excimer laser annealing (ELA) treatment on SRO/SiO₂ superlattice samples produces defect related PL band at 450-550 nm. Furthermore, in the case of SRO/SiO₂ superlattice samples treated by RTA (abovementioned parameters) prior to ELA treatment, the intensity of PL related to Si-nanostructures was only reduced.

Next, the study on the size control of Si nanocrystals by rapid oxidation method using rapid thermal annealing (RTA) process was carried out. The annealing treatment comprises of two RTA steps: RTA at temperature of 1000°C, in N₂ ambient, for 2 minutes and followed by rapid oxidation, which is RTA at temperature of 800°C, in O₂ ambient from 2 to 10 minutes. Upon oxidation up to 10 minutes, the PL peak wavelength was blue-shifted to ~680 nm. In addition, PL intensity was also increased by a factor of 3. The rate of PL peak shift in this experiment is relatively much faster than that in other reported works. The key difference is that the samples were less densified prior to oxidation because of rapid annealing process. It was also shown that the PL peak-shift depends very much on the initial average of Si-nanostructures. Further enhancement of PL intensity without severe PL peak shift was demonstrated by annealing the oxidized samples at lower temperature (600°C).

Subsequently, based on the development of Si-nanostructure above, Si nanostructure-sensitized Er related PL were studied, developed and optimized. The Er:SRO/SiO₂ superlattice structures were developed to study the sensitizing effect of Si nanostructures on the emission of Er ions in SiO₂ matrix. The Er concentration in SRO layer was set at ~1.2 at.%. All samples were treated by the RTA process at temperatures ranging from 500 to 1000°C in N₂ atmosphere for 2 minutes. The PL measurement of the sample was carried out using He-Cd laser emission line at 442 nm, which is non-resonant to the energy levels of the Er. Defect passivation was carried out by annealing in forming gas (5% H₂:N₂) environment at 500°C for 1 hour on the samples which have been annealed by RTA process. Based on the RTA process and defect passivation of the samples, it is shown that at RTA temperature of 700°C or below, defect-mediated excitation is responsible for Er emission peaked at 1.53 μm. For samples annealed at temperatures 850°C and above, defect passivation is important to enhance the energy transfer from Si nanostructure to Er ions. The enhancement of the energy transfer is achieved by the reduction of the competing non-radiative recombination centres

through the hydrogen passivation. The effect of Si nanostructure size on Er emission was also studied. It is found that the optimum size of Si nanostructure for energy transfer to Er is ~3.5 nm.

In view of implementing the developed superlattice samples for light emitting devices, a more efficient structure is necessary. One of the approaches investigated in this work is by fabricating the air-hole triangular lattice photonic crystal (PC) slab structure penetrating into the emitting layer. The PC slab structure was fabricated using deep-UV etching technique. Such penetrating PC slab structure was designed to produce more enhanced light extraction and modification of spontaneous emission than that located on top of the emitting layer.

The excitation and emission of the structure were performed vertically. PL intensities of the PC slab samples were indeed enhanced by several times and their spontaneous emissions were modified as compared to those of the un-patterned sample. This can possibly be attributed to several enhancement mechanism based on: (1) coherent Bragg scattering of the internally trapped light in the PC structure, including Photonics bandgap (PBG) effect and strong coupling to the high-Q leaky or resonant radiant modes and (2) quantum electrodynamic effects, i.e. Purcell enhancement of spontaneous emission and electromagnetic field distribution in the structure.

In summary, the SRO/SiO₂ and Er:SRO/SiO₂ superlattice structure developed and optimized using a low thermal budget annealing, such as RTA process and hydrogen passivation show PL emission bands around 680-800 nm and 1530 nm, respectively. To increase light extraction and modify the spontaneous emission of the emitting layer for light emitting diode (LED) application, PC slab penetrating both structures have been fabricated. The PL enhancement, indicating more efficient light extraction, paves a way to implement Si-based light emitting structures in the future.

List of Abbreviations

CB	Conduction band
CCD	Charge coupled device
ELA	Excimer laser annealing
ET	Energy transfer
FG	Forming gas
FTIR	Fourier transforms infrared
IC	Integrated circuits
IR	Infrared
LED	Light emitting device
LO	Longitudinal Optics
NIR	Near infrared
PC	Photonic crystal
PECVD	Plasma enhanced chemical vapour deposition
PL	Photoluminescence
PLE	Photoluminescence excitation
PMT	Photo multiplier tube
RTA	Rapid thermal annealing
SE	Spectroscopic ellipsometry
SEM	Scanning electron microscopy
SRO	Si-rich oxide
TEM	Transmission electron microscopy
TO	Transverse Optic
UV	Ultraviolet
VB	Valence band
VIS	Visible
XPS	X-ray photoelectron microscopy
2D	two-dimensional

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Chapter 1

Introduction

1.1 Motivation

1.1.1 Silicon photonics

To this present day, the Silicon (Si) technology is able to maintain the Moore's Law which states that the complexity for minimum component costs to roughly double per year [1-1]. Indeed, over the years, the success of Si technology has been demonstrated by dramatic improvement of the performances of the integrated circuits while maintaining the exponential decrease of per-component manufacturing cost. This success owes to the continuous effort to scale down transistor size which enables production of more powerful chips at affordable price. In terms of fabrication process, the smaller transistor size also drives down the manufacturing cost of chips with any given complexity because more identical copies can be simultaneously made at nearly the same cost.

However, increasing density of transistors on a chip requires increasing number of interconnecting wires to link those transistors together. At present, an electronic chip can contain around 1 km of wiring per cm^2 of chip area. Such long interconnect wires produce significant power waste through resistive heat and worsen RC circuit delay. By scaling down the transistor size, i.e. increasing transistor density, further RC circuit delays will be a more dominant problem of overall performance of future integrated circuits. This is well known as "interconnect bottleneck" issue. The emergence of copper (Cu) to replace Aluminum (Al) as interconnect wires and reduces the resistance of the wires by nearly half still allow further increase of transistor density on a chip [1-2], [1-3]. In addition, research works in low-k dielectric may postpone the interconnect bottleneck issue in the near future [1-4].

Nevertheless, a strong need for a long term solution which enables further scaling of integrated circuits in the future is imminent. This is where photonics plays its role. Photonics systems such as lasers, modulators, optical waveguides and photo-detectors could be used to replace interconnecting wires between regions of integrated circuits [1-5], [1-6]. The advantages of this approach are eliminating delay, cross talk, and power dissipation in signal processing. However, there are still several challenges to be overcome. At the moment, one of interest is in Si photonics, which is essentially the integration of photonic and electronic functionalities on a common Si substrate using mature Si processing.

There are several properties of Si which are suitable and applicable for both electronic industry and photonics fields. For examples, Si is abundantly available and has high thermal conductivity, high optical damage threshold, and good mechanical strength [1-7]. Furthermore, for photonic applications, Si has a high refractive index (~ 3.5) [1-8], as well as good low intrinsic loss in the infrared (IR) wavelength spectrum (1.1-7 μm) [1-9]. These properties make Si suitable for high density photonic devices, such as, low loss high index contrast planar waveguides [1-10],[1-11], optical switches [1-12],[1-13], and modulators [1-14],[1-15].

However, the light emission efficiency of Si is known to be inefficient that many consider photonic circuit beyond the reach of Si. By nature, Si has indirect bandgap property, which means the minima of conduction and valence bands of Si material do not occur at the same crystal momentum, thus leading to an extremely inefficient emission [1-16]. This natural property has hampered the progress of integrating photonic devices on Si because light emitting device is also one major part in integrated photonic structure. There are a lot of efforts to integrate III-V materials, e.g. GaAs and InGaAs, which are widely used as light sources in infrared (IR) communication wavelength, on Si substrate with certain degree of success [1-17]-[1-19]. However, in this project, the author addresses the light emission of Si nanostructures and its sensitizing effect on Er emission at optical communication wavelength of 1.55 μm .

1.1.2 Light emission of Silicon nanostructures

It is only in the early 1990s that a relatively much stronger emission was observed from Si nanostructures in the form of porous Si nanocrystals [1-20],[1-21] and Si-nanocrystal embedded in SiO_2 [1-22]-[1-25]. Si nanostructures improve the radiative recombination rate which would otherwise be very much lower in bulk Si. The photoluminescence (PL) band, attributed to excitonic recombination in the Si nanostructure [1-24]-[1-26], is observed in the visible to near infrared (NIR) spectra. The origin of the Si nanostructures related PL is generally attributed to two mechanisms: quantum confinement effect (QC) and surface defects [1-26]-[1-30]. A more detailed review of the PL mechanism will be discussed in Chapter 2. In this project, Silica (SiO_2) was chosen as the embedding (host) material.

In view of the light-emitting application, several important and relevant characteristics of Si nanostructures, such as nanostructure lifetime, correlation between PL peak and average nanostructure size, as well as size distribution, have also been reported with varying degree of results [1-31]-[1-33].

However, the research work on Si nanostructures still faces several challenges, as follows:

1. Size controllability of Si nanostructures (nanocrystals or amorphous nanostructures) to control emission peak via deposition and post-deposition process. In bulk Si rich oxide (SRO) film,

high temperature annealing at prolonged time is necessary to effectively form Si nanocrystals with efficient emission efficiency. The drawback of simple bulk SRSO film is that the size distribution of Si nanocrystals is very large, indicated by large full-width half maximum (FWHM) of Si nanocrystals related photoluminescence (PL) [1-34], [1-35]. Recently, Zacharias et al. [1-36] reported that certain control of Si nanocrystals size distribution can be achieved using reactively evaporated SiO/SiO₂ superlattice structure. In their work, upon annealing at 1100°C for 1 hour, an optimum PL intensity was observed. By controlling SiO layer thickness during deposition process, controlled size of Si nanocrystals can be achieved. On the basis of this result, the author adopted this superlattice approach. This will be described in more detailed in Chapter 4. It is also important to note that size controllability of Si nanostructures by rapid oxidation process has not been well studied. This particular issue will also be addressed in Chapter 5. With oxidation method, Si-nanocrystals size can be tailored oxidation temperatures and time.

2. High thermal budget process to promote growth of Si nanostructures. The annealing process at high temperature of 1100°C for a prolonged time is generally applied to optimize the formation of well-passivated crystalline Si nanostructures. In this work, the author investigated the low thermal budget processes, such as rapid thermal annealing (RTA) and excimer laser annealing (ELA) techniques to promote the formation of Si nanostructures. Furthermore, to enhance the Si nanostructures related emission, defect passivation by annealing in forming gas could be applied. The study of the low thermal budget processes and defect passivation will be presented in Chapter 4, 6, and 7.

1.1.3 Silicon nanostructures as sensitizers for Erbium

The ever increasing demand for large bandwidth information system has driven a concerted effort on the development of telecommunication technology operating in the optical wavelength region at 1.55 μm . Therefore, it is desirable for small integrated photonic devices to operate in IR wavelength spectra because it offers relative ease in interfacing with bulkier optical communication system.

In the past few years, some success in the development of Erbium (Er) for integrated photonic devices has been reported. The materials of interest are generally oxide based, such as SiO₂ [1-37]-[1-40], Er:SiO₂:TiO₂[1-41], Er:P₂O₅ [1-42],[1-43], ZrO₂[1-44],[1-45], and Al₂O₃ [1-46],[1-47], because of its good environment for optically active Er ions (Er³⁺). However, the implementation of Erbium doped in oxide materials for the small integrated optical devices and on-chip optical interconnect applications has several obstacles as follows:

1. The small absorption cross section of Er, in the range of $\sim 10^{-21}$ - 10^{-20} cm² [1-48], requires either a large concentration of Er or long active (Er-doped) region. For the former case, the Er concentration solubility in silica is very small, in the range of ~ 0.1 at.%, to avoid clustering of Er which hampers the gain build up due to up-conversion effect [1-48]. In the latter, the need for long active region poses challenges in device minimization as well as other Er-Er interaction such as upconversion and excited state absorption.

2. The direct excitation of Er has to be in resonance with any of the higher lying energy level of Er, thus restricting the optical pumping to laser operating at certain resonant wavelength such as 980 nm, which is resonant to $^4I_{11/2}$ transition and 1480 nm, which is resonant to $^4I_{13/2}$ transition [1-38]-[1-48]. The usage of laser pumping is rather costly. Furthermore, lasers operating at these wavelengths (1480 and 980 nm) are commonly based on III-V materials and the implementation of III-V materials as pump of Er-doped structure poses the difficulty of integration with Si, which is a group IV material.

Despite all these limiting problems related to Er doped oxide materials, the discovery of light-emitting Si nanostructure gives a fresh momentum on the Er doping into miniature photonic devices. Several encouraging results have indicated that Si nanostructure is a promising candidate as Erbium sensitizers. The reported emission wavelength (700-950 nm) and lifetime of Si nanostructures (ranging from 1-100 μ s), depending on the preparation method [1-49]-[1-51], is enough to facilitate energy transfer from Si-nanocrystals to Er. Fujii et al. [1-52] reported that in the presence of Si nanocrystals enhanced the effective excitation cross section of Erbium. Having a broad excitation spectrum, the Si nanostructures offer flexibility of optical pumping sources and wavelengths for Er emission. However, at present, there are still several conflicting results in the development works of Si-nanostructure sensitized Er, as follows:

1. The dependence of Er emission on the Si nanostructure size has not been clarified. In most of the literatures, the Si nanostructures sensitized Er ions embedded in SiO₂ materials are usually fabricated by annealing of bulk Er doped Si-rich oxide (Er:SRO) thin films [1-53]-[1-55]. After annealing process, the large size distribution of Si nanostructures makes the proper study on the size effect of the energy transfer to Er difficult. Energy transfer between closely neighbouring Si-nanostructures with different sizes results in the energy transfer from smaller nanostructures to larger nanostructures, which competes with the energy transfer from Si nanostructures to Er ions [1-56], [1-57]. Therefore, to better understand the effect of Si nanostructures size on Er emission, an Er doped Si-rich oxide/SiO₂ (Er:SRO/SiO₂) superlattice structure would be a more suitable approach due to the possibility of controlling the size of Si nanostructures. In this project, the author developed Er:SRO/SiO₂ superlattice samples and this will be discussed in Chapter 6.

2. High thermal budget annealing process (at high temperature long annealing time) is usually employed to promote Si nanostructure and passivate any competing non-radiative recombination centers [1-53]-[1-55],[1-56]. In this work, however, the author studied the low thermal budget treatment process in the form of rapid thermal annealing (RTA) process to promote Si nanostructures. To study the effect of hydrogen passivation on the Er emission, annealing in forming gas was also implemented.

1.1.4 Light Enhancement by photonic crystal slab structure

Generally, in simple light emitting uniform slab structures with effective refractive index, $n_g = n / n_{air}$, it is estimated that only $\sim 1/(4n_g^2)$ of the light emitted is radiated out through the top or bottom, whereas the rest of the light simply remain trapped in the slab film through total internal reflection (TIR) [1-57]. Light output efficiency of a light emitting uniform slab structure is inefficient especially when the refractive index is larger than the surrounding medium (e.g. air) [1-57], [1-58]. One of the approaches to enhance the light output efficiency is to fabricate two dimensional (2D) photonic crystal (PC) slab structures [1-57]-[1-60]. This will be discussed in more detail in Chapter 2. In this work, Er doped Si-rich oxide/SiO₂ superlattice based 2D PC slab structures have been fabricated and characterized. The study of the effect of photonics crystal structure properties, such as photonic band gap (PBG) and leaky modes, on the enhancement of photoluminescence (PL) from Si nanostructures as well as Er, is presented in Chapter 7.

With these considerations, the Thesis work entitled “Development of Silicon Nanostructures as Light Emitter and Sensitizer for Erbium Emission” is presented.

1.2 Objectives

The objective of this work is, firstly, to achieve good control of Si nanocrystals using low thermal budget annealing of Si-rich oxide/SiO₂ (SRO/SiO₂) superlattice structures, secondly, to develop Er:Si-rich oxide/SiO₂ superlattice structures to study the energy transfer from Si nanostructures to Er for light emitting devices in optical communication wavelength, 1.55 μm , and thirdly, to enhance the light output efficiency of the annealed SRO/SiO₂ and Er:SRO/SiO₂ superlattice light emitting layer using two-dimensional (2D) photonic crystal (PC) slab structures.

The details are outlined as follows:

1. To develop well controlled Si nanostructures size in SiO₂ matrix using radio frequency (rf) magnetron sputtered Si-rich oxide/SiO₂ superlattice structure. This was achieved by optimizing

several parameters, such as excess Si concentration in Si-rich oxide layer, Si-rich oxide layer thickness and low thermal budget post-deposition treatments, including rapid thermal annealing (RTA) and excimer laser annealing (ELA) processes. The study of the effects of RTA and ELA processes on the SRO/SiO₂ superlattice structures is discussed in Chapter 4. The review of the deposition methods are discussed in Chapter 2.

2. To develop Erbium doped Si-rich oxide/SiO₂ superlattice structure and demonstrate the non-radiative energy transfer from Si nanocrystal to Erbium ions. The effects of Si nanostructure size, rapid annealing temperature and passivation on Er emission at 1.55 μm in this structure were studied. Using energy transfer mechanism, the excitation wavelength is not necessarily to be resonant with $4f$ energy levels of Erbium ions.

3. To fabricate 2D PC slab structure to demonstrate enhancement of PL emissions from Si nanostructures in visible wavelength (700-900 nm) and Er at infrared (1.55 μm) spectra.

1.3 Major Contributions of the Thesis

The major contributions of this Thesis are summarized below:

- i. A well controlled size of Si nanocrystals has been successfully developed using rf magnetron sputtered Si-rich oxide/SiO₂ (SRO/SiO₂) superlattice structure. The optimum Si concentration in SRO layer in this work is $\sim 46\%$. A low-thermal budget method in the form of rapid thermal annealing (RTA) process in N₂ environment at 1000°C for 2 minutes was implemented to produce PL emission related to SRO/SiO₂ superlattice structures. Si nanocrystals related PL bands were observed at 768, 802, and 815 nm for samples with SRO layer thicknesses of 3, 4 and 5 nm. In addition, two oxygen deficiency defect related PL bands at 400 nm and 515 nm were also observed. The details will be presented in Chapter 4 [Paper-I].
- ii. The author demonstrated that annealing of rapid thermal annealed (in N₂, at 1000°C for 2 minutes) SRO/SiO₂ samples in forming gas (5%H₂:N₂) at 500°C for 1 hour enhanced the Si-nanocrystal related PL emission intensity by a factor of ~ 8 . This was achieved by hydrogen passivation of defects such as Si dangling bonds on the surface of Si-nanocrystals which was not completely cured during the RTA process. Furthermore, it was also demonstrated that the PL intensities of the SRO/SiO₂ superlattice samples treated using the RTA process and annealing in forming gas were higher than those of the samples annealed using conventional annealing process in N₂ environment at 1100°C for 2 hours. The details will be presented in Chapter 4.
- iii. The author has also demonstrated the two-step rapid annealing technique to control and optimize the peak and intensity of Si nanocrystal related photoluminescence. This can be explained

because rapid annealed Si-rich oxide/SiO₂ superlattice sample were not fully densified. At 2 minutes rapid annealing, only Si nucleation occurred and surfaces of Si nanocrystals were therefore not yet well passivated. Such rapid oxidation time (1-10 minutes) is much faster than oxidation rate of Si nanocrystal reported by other researchers. The details will be presented in Chapter 5 [Paper-II].

iv. Having established a well controlled Si nanocrystal emission, the author improved the PL intensity without severely causing PL peak shift of the oxidized Si nanocrystals by annealing the rapidly oxidized sample in air environment at 600°C (lower temperature) in 30 minutes. This effectively increased the PL peak intensity further by a factor of 2-9 depending on the initial Si nanocrystal average size. The details will be presented in Chapter 5 [Paper-II].

v. In order to realize Si-nanostructures sensitized Er emission at 1.53 μm and to study the size dependence of energy transfer from Si nanostructures to Er ions, the author introduced Er dopants in the SRO layer of Er:SRO/SiO₂ superlattice structures. In this work, the Er concentration at 1.2 at.% were studied and optimized using RTA process and hydrogen passivation by annealing in forming gas (5%H₂:N₂). The RTA process was done in N₂ for 2 minutes at various temperatures, ranging from 500°C to 1000°C. The effects of RTA temperature with and without hydrogen passivation on the Er emission of the samples were also studied and analyzed. It was concluded that without hydrogen passivation, the optimum temperature is at 850°C, at which defect related indirect excitation was largely responsible for Er emission. On the other hand, with hydrogen passivation, the optimum temperature is 1000°C, at which Si nanostructures related energy transfer mechanism was largely responsible for Er emission. For all passivated samples, the optimum Er emission intensity was observed for samples with Si nanostructures size of 3.5 nm. The details will be presented in Chapter 6 [Paper-III].

vi. The author demonstrated that Er PL emission intensity of the sample annealed using the RTA process followed by hydrogen passivation (described in part v) to be comparable with that of the sample annealed in N₂ at 850°C for 8 hours. This suggested that rapid annealing and passivation method was proven to be a good low thermal budget alternative. The details will be presented in Chapter 6 [Paper-III].

vii. The author developed and fabricated SRO/SiO₂ and Er:SRO/SiO₂ superlattice based photonic crystal structures using deep-UV technique to enhance the light output intensity in the vertical direction for PL emission at 700 nm and 1.53 μm . The photonic crystal structures were designed to penetrate the light emitting layers. Enhancements by a factor of 4 of Si nanostructures and Er emissions intensity have been demonstrated. The details will be presented in Chapter 7 [Paper-IV].

From all the above contributions, several papers have been published and prepared for submission as follows:

[Paper-I] Samson T. H. Silalahi, H.Y. Yang, K. Pita, and Yu Mingbin, “Rapid Thermal Annealing of Sputtered Silicon-Rich Oxide/SiO₂ Superlattice Structure”, *Electrochemical and Solid-State Letters*, 12 (2009) K29-K32

[Paper-II] Samson T. H. Silalahi, H.Y. Yang, Q.V. Vu, K. Pita, Yu Mingbin, “Size control of Sputtered Silicon-rich Oxide Superlattice Structure by Two-step Rapid Thermal Annealing”, (accepted for publication in *Applied Physics A: Material Science & Processing*)

[Paper-III] Samson T. H. Silalahi, Rui Chen, Q.V. Vu, K. Pita, H.D. Sun, and M.B. Yu, “The Effects of Rapid Annealing and Passivation of co-sputtered Er:Si-rich Oxide/SiO₂ Superlattice Structures” (submitted to and under review in *Applied Physics Letters*)

[Paper-IV] Samson T. H. Silalahi, Yu Mingbin, and K. Pita “Un-doped and Erbium-doped Si-rich Oxide Superlattice based Photonic Crystal Slab Structures” (prepared for submission)

1.4 Organization of the Thesis

This thesis consists of nine chapters which will be described below.

Chapter 1 is an Introduction, comprising four sections: Motivation, objectives, Major contribution of the Thesis, and the Organization of the Thesis.

Chapter 2 is “Literature Review”. In this chapter, the author firstly presents a review on the role of the Si nanostructure and its energy transfer to Erbium for photonics application, especially in the optical communications field. Subsequently, the author describes various fabrication techniques of erbium doped Si nanostructures such as Si implantation, evaporation, chemical vapour deposition, and co-sputtering.

In Chapter 3, titled “Characterization Techniques”, the author explains various characterization techniques used in the work.

In chapter 4, titled “Development of Si-rich Oxide/SiO₂ Superlattice Structure”, the author presents the development of Si-rich oxide/SiO₂ (SRO/SiO₂) superlattice structures using rapid thermal annealing (RTA) process. The study of hydrogen passivation treatment on the PL emission of rapid annealed samples and the comparison of the obtained PL intensity with that of samples treated using long conventional process are presented. The effects of Excimer laser annealing (ELA) process on the PL emission of Si nanostructures are also discussed.

Chapter 5 titled “Size Control of Silicon Nanocrystal by Two-step Rapid Annealing Treatment” presents the study on the two-step rapid thermal annealing (RTA) process, consisting of RTA in N₂ environment followed by rapid oxidation process in O₂ environment. The study of the

effects of rapid oxidation on the PL intensity and Si nanocrystal sizes of the samples is presented. Further enhancement of Si-nanocrystals related PL intensity using long annealing in atmospheric ambient is also presented.

In chapter 6, “Development of Erbium doped Si-rich Oxide/SiO₂ Superlattice Structure”, the author elaborates the study the effects of the RTA process and hydrogen pasivation on the Er PL emission spectra at 1.55 μm . The study of the size-dependence of Er emission for hydrogen passivated samples is also presented.

In chapter 7, “Light Enhancement using Two-Dimensional Photonic Crystal Slab Structures”, the development work of a photonic crystal slab structures based on SRO/SiO₂ and Er:SRO/SiO₂ superlattice structures is presented.

Chapter 8 titled “Other Work: Development of Sputtered Silicon Oxynitride Material” presents an additional work on the development of Si oxynitride (SiON) thin films using reactive sputtering technique. Characterizations of refractive index the SiON thin films and the propagation loss of SiON slab waveguides are presented.

Finally, in chapter 9, “Conclusions and Recommendations”, the author concludes the Thesis and gives recommendations for future works, based on the results in this work.

Chapter 2

Literature Review

2.1 Introduction

Silicon photonics discipline has experienced a tremendous progress and development in the past two decades due to the possibility of utilizing the already mature silicon process technology [2-1], [2-2]. Figure 2.1 shows the basic building blocks of Silicon (Si) photonics, which are optical components, such as light emitters, waveguides, modulators, photo-detectors and interconnect, and digital electronic chips on Si platform that can be manufactured using Si process technology [2-3].

Figure 2.1 The integration of various Si photonic components on silicon substrate [2-3]

Motivated by its potential benefit as a long term solution of interconnect bottleneck issue in the electronic integrated circuits [2-4],[2-5], many research works have been carried out to realize various Si-based photonic components such as modulators [2-6]-[2-8], high index contrast optical

passive waveguides [2-9]-[2-13], and photo-detectors [2-14]. However, despite all the progress made over the past decades, the lack of efficient light emission from Si has eluded the realization of fully integrated silicon photonics circuit.

Silicon (Si), having an excellent transparency from 1.1 μm to about 7 μm [2-15], is a strong candidate for low-loss optical waveguide, especially in the optical communication window centered at 1.55 μm . Furthermore, with a high refractive index (~ 3.4 at 1550 nm), index contrast waveguide structures which promise device area minimization due to possible bending radius of 1.5 μm can be realized [2-11], [2-16]. Si photo-detectors operating at wavelengths below 1000 nm has been commercially available for several decades. The challenge is to apply Si for optical fiber communication bands around 1300 nm and 1550 nm because the photon energies of these wavelengths are less than bandgap energy of silicon [2-17]. Nevertheless, Germanium (Ge) material, which is a group IV material, has emerged as strong candidate for detectors and excellent results approaching III-V materials based detectors in terms of speed and responsiveness have been reported [2-18]-[2-21].

Figure 2.2 E-k diagram of bulk crystalline silicon (c-Si) [2-22]

On the other hand, Si has never been considered a natural candidate for efficient light emitter. This is related to the fundamental property of Si, which is the indirect band gap material. In Figure 2.2, the schematic band diagram of this indirect bandgap is shown to explain the problem. As shown in Figure 2.2, the minima of conduction band and the maxima of valence band do not occur at the same crystal momentum and therefore, in order for radiative recombination to occur, phonon assistance is required [2-22]. Since the probability of the radiative recombination in Si is very low, the radiative lifetime is long, in the order of milliseconds. Both electrons and holes move around in the Si crystal lattice and therefore they have a high probability to recombine fast non-radiatively (in the range of nanoseconds) once they encounter trapping centres. The internal quantum efficiency (the ratio of the probability that an excited e-h pair recombine radiatively) of emission of Si is only $\sim 10^{-6}$ [2-23]. Such poor efficiency has rendered Si unfavorable for light emission despite its remarkable contribution in the area of microelectronics. However, a relatively new approach of obtaining light emission from Si nanostructures in the visible range has been demonstrated. This new approach has reignited the interest on realizing Si based light emitting devices [2-24], [2-25]. Furthermore, such nanostructures also have the potential use as sensitizer for Er emission at $1.55\ \mu\text{m}$ [2-26], [2-27]. Indeed, Si nanostructures have paved a new path for realizing a more efficient light emission from Si materials leading to a possible full integration of Si photonics devices in the future. At the moment, however, the challenge still lies on the level of material physics and processing to produce an efficient and low cost light emitting Si-nanostructures.

In section 2.2, a review on the development of Si nanostructure for light emission in the visible wavelength spectrum is presented. In this section, the author elaborates various important and relevant results on emission of Si nanostructures. Furthermore, the author will discuss the development of Si nanostructures as Er sensitizers for optical communication wavelength at $1.55\ \mu\text{m}$. In section 2.3, the author presents a review on several photonic structures and devices which are based on the Si nanostructures and Si nanostructures sensitized Er system for application in the visible and IR wavelength, respectively. And lastly, in section 2.4, various kinds of deposition methods to produce the light emission are discussed.

2.2 Light emission from Si nanostructures

In the previous section, the author has explained the fundamental problem in getting light emission from bulk Si materials. However, during the past decade, the light emission from Si nanostructures embedded in solid dielectric material has successfully been demonstrated. In addition, sensitizing effect of Si nanostructures on Er emission at $1.55\ \mu\text{m}$ has also been explored. The development works on these two material systems are discussed in the following sections.

2.2.1 Silicon nanocrystals

As the size of Silicon (Si) decreases to nanometer scale, the band gap becomes wider than that of bulk Si, ~ 1.1 eV. Furthermore, depending on the embedding material and size, upon optical excitation at near UV or visible wavelengths, Si nanostructures, have been demonstrated to emit light in the visible to near infrared spectrum, ranging from 400 to 1000 nm. The development of silicon nanostructures was initiated by the observation of visible photoluminescence of porous Si nanostructure [2-28]-[2-30] and subsequently followed by a greater interest on more chemically stable structures, such as Si nanostructures embedded in silica (SiO_2) [2-31]- [2-35].

2.2.1.1 Porous silicon

In early 1990s, extensive works were focused on studying the porous Si (p-Si) which has exhibited luminescence in the visible range. Porous silicon is formed by electrochemical anodization of Si in an HF electrolyte. The solution employed is typically aqueous 50% HF mixed with ethanol [2-28], [2-30], [2-36]. Several important factors involved in the fabrication of porous Si such as HF concentration, current density, anodization time, temperature, as well as Si doping type, has been well reviewed by Smith et al. [2-38]. The sequence of processes used in this technique results in Si skeleton composed by the interconnected Si nanocrystals or thin Si wires [2-38].

(a)

(b)

Figure 2.3 (a) PL spectra of porous Si samples with different average size before (left graph) and after (right graph) exposure to oxygen ambient, as measured by Wolkin et al. [2-39]
(b) The calculated conduction and valence bands for H-passivated and oxygen bonds on the surface of Si nanocrystals [2-39].

In 1999, Wolkin et al. reported the work on the effect of ambient on the photoluminescence (PL) spectra of porous Si [2-39]. Figure 2.3(a) shows the measured PL spectra of various porous Si samples for different sizes of nanocrystals before (left graph) and after exposure (right graph) in oxygen ambient. Prior to exposure in O_2 ambient, the Si nanocrystals are H-passivated whereas upon exposure to O_2 ambient, large presence of oxygen bonds exists on the Si nanocrystals surface. In Figure 2.3(a), samples with H-passivated Si nanocrystals are labelled according to the colours of their

emission wavelength, ranging from blue (size of ~2 nm) to red (size of ~4 nm). The PL peak red-shift upon exposure to O₂ ambient is more significant as the size of nanocrystals decreases. To explain this observation, in Figure 2.3(b), Wolkin et al. [2-39] presents the calculated conduction and valence band energy levels for H-passivated nanocrystals, as well as the calculated energy levels due to the presence of a trapped electron and a trapped hole at a Si=O bond at the Si nanocrystals surface, for different sizes. As the size of nanocrystals decreases, the band-gap increases due to the quantum confinement effect and the Si=O levels appear in the band-gap. In Figure 2.3(b), Zone I, Zone II and Zone III represent the regions in which the Si-nanocrystal related emission involves dominantly band-to-band, a trapped electron, and both trapped electron and hole, respectively [2-39]. The significance of this work is providing a semi-empirical approach for qualitative explanation on the interplay between quantum confinement effect and surface bonding on the PL peak wavelength of Si nanocrystals.

However, p-Si nanostructure has a limitation in terms of its sensitivity in atmospheric ambient. Wolkin et al. [2-39] reported a consistent red-shift of visible PL peaks when porous Si samples were moved from pure argon ambient to oxygen ambient. This sensitivity of the porous silicon can be used to form active material of gas and biosensors [2-40], [2-41]. However, the instability of the porous Si system with time (ageing effect) poses a limitation on the reliability of the materials for practical devices.

2.2.1.2 Silicon nanocrystals embedded in SiO₂

The formation of porous Si by electrochemical etching has been well studied, but its sensitivity and stability issues (ageing affect) have hindered its potential implementation on practical devices. Such limitations can be alleviated by forming silicon nanocrystals embedded in a dielectric matrix. One of the popular materials chosen as embedding matrix is Silica (SiO₂) because it is most widely used material in Si process technology [2-42],[2-43].

Extensive and comparative studies on the Si nanocrystals embedded in SiO₂ covering several aspects such as fabrication processes [2-44]-[2-51], optical [2-45]-[2-48], electrical [2-49], [2-50], and microstructure properties [2-51], has provided excellent information and literatures for fabricating devices as well as realizing the potential use of the Si-nanostructures for various applications [2-45]-[2-51]

Figure 2.4 The enlargement of the bandgap of a Si nanocrystal with shrinkage of size, which is known as the quantum confinement effect. CB and VB represent conduction and valence bands of bulk Si, respectively. The Si-nanocrystals gap is defined as the distance between the first higher lying energy level and the first lower lying energy level. The bandgap of SiO₂ host is around 9 eV [2-50].

Figure 2.4 shows the simplistic theoretical model describing the enlargement of the bandgap of a Si nanocrystal with shrinkage of size of Si material due to the quantum confinement effect [2-50]. This model, although simplistic, has been the basis of some theoretical models used to explain the absorption and emission related to Si nanocrystals.

Figure 2.5 The optical bandgap of Si nanostructures and porous Si obtained from optical absorption (unfilled symbols) and PL (filled symbols) [2-52]. The graph (solid line) is the fitting by theoretical model.

Figure 2.5 shows the compilation of absorption (unfilled symbols) and PL (filled symbols) of Si nanocrystallites and porous Si by Allan et al. [2-52]. In this figure, it is observed that theoretical models based on quantum confinement effect are able to follow the trend of optical absorption of Si nanocrystals. However, there is a large Stokes shift, i.e. discrepancy between optical absorption and measured PL emission data (see Figure 2.5). To explain such occurrence, several authors have proposed a model involving the radiative emission centers located at the Si/SiO₂ interface. Indeed, it has been demonstrated that the silicon-oxygen bonds (Si=O) introduces a deep level inside the gap, which could play an important role in the PL emission and explain the disagreement between the PL emission and absorption measurements shown in Figure 2.5 [2-39], [2-52]. From Figure 2.5, it can be seen that PL emission band are indeed size-dependent with surface effects becoming more dominant when the size of nanocrystals decreases. Similar observation has also been shared by Wolkin et al. [2-39] which has been explained in section 2.2.2.1. This mechanism will be used in Chapter 4 to explain the PL spectra of the samples developed in this work.

To achieve a well controlled PL emission peak, it is desirable to have a fabrication method which can control the size of Si nanocrystals, i.e. relatively narrow size distribution of Si nanocrystals. The common fabrication of Si-nanocrystals by thermal annealing bulk Si-rich oxide (SRO) does not produce good uniformity and reproducibility of Si nanocrystals [2-45]-[2-50], [2-52]. The strong dependence of the size and distribution of Si nanocrystals on the fabrication method and thermal annealing makes it difficult to control the PL emission peak of Si nanocrystals. Furthermore, using this approach, the PL intensity and nanocrystals size are strongly correlated to the excess Si

concentration. Therefore, using simple bulk SRO sample, it is very difficult to obtain controllable PL peak wavelengths and comparable PL peak intensities for different sizes of Si nanocrystals.

Figure 2.6 (a) The PL spectra of samples with different Si-nanocrystals size (b) The well arranged of Si nanocrystals with average size with small distribution (3.3 ± 0.5 nm) formed by thermal annealing of SiO/SiO₂ superlattice structure reported by Zacharias et al. [2-53]

The size dependence of PL peak wavelength means that a more uniform Si size distribution is preferred if we are to study more properly the fundamental properties of Si-nanocrystals, such as size-dependence of Si-nanocrystals related PL peak wavelength as well as absorption cross section. In 2002, Zacharias et al. [2-53] demonstrated that a strong PL intensity of Si nanocrystals independent of size of nanocrystals can be realized by annealing of the reactively evaporated SiO/SiO₂ superlattice structure in N₂ at 1100°C for 1 hour, as shown in Figure 2.6(a).

In their work, the SiO/SiO₂ superlattice samples have SiO layers with thicknesses from 1 nm to 3 nm. The SiO/SiO₂ superlattice structures consist of 46-92 periods of alternating SiO and SiO₂ layers. In Figure 2.6(b), the superlattice arrangement of Si nanocrystals with relatively narrow size distribution is shown. The size of Si nanocrystals is dependent largely on the size of as-deposited SiO layer and the narrow size distribution is attributed to the roughness of SiO/SiO₂ interfaces in the as-deposited samples, which can be controlled to below 0.5 nm. With relatively long annealing, comparable PL intensities of samples with different average sizes of nanocrystal have also been demonstrated. Such independence is not possible using by bulk Si-rich oxide because the density and

size of nanocrystals solely depend on excess Si concentration. Other studies such as the phase separation of SiO/SiO₂ superlattice structure have also been reported by L. X. Yi et al. [2-54]

Despite all the progress reviewed here, as mentioned in the Chapter 1, several issues such as the size controllability and high thermal budget has not been adequately addressed. Furthermore, in terms of fabrication process of Si-nanostructures, a high thermal budget process in the form of long annealing at high temperatures in inert gas is commonly used to form, crystallize, and passivate the surface of Si nanostructures. However, it would be economically favorable if low thermal budget process, such as rapid thermal annealing (RTA) and excimer laser annealing (ELA) could be implemented. This is possible based on the empirical study of PL behaviour over annealing time reported by Khriachtchev et al. [2-55] Both annealing methods, RTA and ELA, will be discussed in more detail in section 2.4.4. To improve the PL intensity, surface passivation of Si-nanocrystals will also be discussed in section 2.4.4.

2.2.2 Enhancement of Erbium Emission

In the previous section, Si nanocrystals have been discussed as potential source for visible wavelength which is until now covered by III-V materials (e.g. GaAs) for short distance communication from board-to-board or chip-to-chip. Another wavelength spectrum of interest also exists in infrared (IR) region spanning from 1.3 to 1.6 μm , which is the maximum transparency region of silica based optical fiber [2-56], [2-57]. Silica optical fiber has been successfully implemented for long-haul optical transmission medium due to the emergence of Erbium doped Fiber Amplifier (EDFA) structure.

Figure 2.7 The schematic representation of intra-4f energy levels diagram of Er^{3+} ions in solid matrix [2-58]. (a) The upward transitions, which indicates the pumping at 1480 nm and 980 nm pump lights, (b) the process of co-operative up-conversions, where the interaction between two excited Er^{3+} ions leads to the population of the higher lying excited energy levels. (c), (d) the excited state absorption (ESA) of a 1480 nm and 980 nm pump lights, respectively.

Erbium (Er) is a well known rare earth material which has one of the emission lines centered at 1.55 μm . Figure 2.7(a) shows the 4f energy levels of Er^{3+} ions in a solid matrix. Several important emission wavelengths, 1.53 μm , 0.98 μm , 0.8 μm , are related to transitions from excited levels $^4\text{I}_{13/2}$, $^4\text{I}_{11/2}$, $^4\text{I}_{9/2}$, to ground state $^4\text{I}_{15/2}$, respectively. In Er, like many other rare earth materials, the 4f electrons are shielded by the 5s and 5p electrons, hence, the energy levels are only weakly perturbed by the ligand field of the host materials. This means that the intra-4f electronic transitions, shown in Figure 2.7(a), are almost independent of the host materials [2-58], [2-59]. For examples, Er emission in different host materials has slightly different emission shapes without observable shifting of emission wavelength [2-60], [2-61], [2-62].

For small integrated optical devices and also on-chip optical interconnect, the light emission at 1.55 μm is usually desired to maintain the ease of integrating and interfacing devices to bulkier long distance system operating at the same wavelength. Several efforts were reported to implement Er for integrated photonic devices. In the past few years, some success especially in the development of Er for integrated photonic devices has been reported. The materials of interest are generally oxide based, such as SiO_2 [2-60],[2-63]-[2-65], $\text{Er}:\text{SiO}_2:\text{TiO}_2$ [2-66], $\text{Er}:\text{P}_2\text{O}_5$ [2-61],[2-67], Y_2O_3 [2-68],[2-69], Al_2O_3 [2-62],[2-70],[2-71], ZrO_2 [2-72],[2-73], because of the luminescence efficiency of fully

oxidized Er ions (Er^{3+}). In general, the abovementioned Er doped oxide materials have been used to develop a miniature version of EDFA, called Erbium doped waveguide amplifier (EDWA). Several EDWAs based on Er ion exchanged silicate or phosphate glass materials and also by Er implanted Al_2O_3 with reported internal gains of 4.1dB/cm and 0.6dB/cm, respectively, have been reported. The role of rare earth co-dopant, such as Yb^{3+} , has also been used to extend the excitation wavelengths and sensitize the Er ions to improve the overall gain of Er. However, the implementation of Erbium doped in oxide materials for small integrated optical devices and on-chip optical interconnect has several obstacles, such small absorption cross-section and requirement of resonant pumping, which have been cited in Chapter 1. In the future, these two problems could potentially be alleviated with the emergence of Si nanostructures as a good candidate for efficient sensitizers for Er emission.

The author will review the development work of Er in Si based materials, such as bulk Si and Si nanostructures embedded in SiO_2 . The mechanisms responsible for the Er emission in each material system will also be discussed in the following sections.

2.2.2.1 Erbium doped in Silicon

It is well known that bulk semiconductors are natural sensitizers for rare earth ions [2-58]. When rare earth ions sit in the semiconductor matrix, they act as point defects which create defect levels in the bulk semiconductor bandgap. Upon optical or electrical excitation, carriers are generated and trapped at these defects, creating bound exciton. Since the exciton has strong spatial overlap with the rare earth, it can recombine by transferring its energy to the rare earth ions through a process called carrier-mediated energy transfer mechanism [2-58].

Due to its large abundance, Silicon (Si) has attracted major interest as Er host. The equilibrium solubility of Er in Si is not well known, but it is estimated to be quite low at 10^{14} - 10^{16} cm^{-3} [2-74]. Therefore, non-equilibrium incorporation methods, such as ion implantation, have been implemented for the incorporation of sufficiently high Er concentration. Annealing treatment is necessary to cure the defects due to implantation.

At low temperature (77K), a relatively strong PL spectra of Er:Si was reported and this is attributed to carrier-mediated excitation (by bound excitons trapped in the Er-related defect level in the Si matrix) [2-75]. At room temperature (300K), the PL peak intensity of Er:Si were effectively quenched [2-76]-[2-77]. Figure 2.8 shows the schematic of the Er-exciton strong coupling to explain the PL quenching of Er doped Si at room temperatures. Upon optical excitation at 532nm, the bound exciton trapped in Er-related defect levels transfer its energy to Er (represented by E). However, because the energy levels of Er and defects levels are quite similar, an energy backtransfer from Er to related defects (represented by B) also occurs and is intensified at room temperature (300K) [2-76],[2-

78]. Therefore, this backtransfer process is responsible for the quenching of Er^{3+} emission by the generation of excitons.

Figure 2.8 Schematic of the excitation mechanism of Er^{3+} in 30 at.% doped amorphous Si. T and D indicate trapping and detrapping of electrical carriers at Er-related localized defect states. E indicates energy transfer to the Er ions; B is backtransfer from Er ions to the defect state [2-78].

To solve this problem, several methods have been investigated, such as: (i) increasing the bandgap of Si so that the energy barrier for backtransfer is increased, or (ii) decreasing the coupling between the exciton and the Er. The bandgap of semiconductor host (Si) is increased by co-doping with oxygen, as reported by Lombardo et al. [2-79]. In their work, the oxygen concentrations in a semi-conducting polycrystalline Si (SIPOS) were varied between 4 and 27 at.% was implanted with $2 \times 10^{15} \text{ Er/cm}^2$. Enhanced PL intensity of Er peaked at $1.53 \mu\text{m}$ was observed and at 27 at.%, the intensity is as half as that in SiO_2 matrix. This indicates reduced backtransfer energy due to larger host bandgap. Photoluminescence excitation spectroscopy showed the Er was excited indirectly, i.e., through photo-carriers in the amorphous semiconductor (bandgap $\sim 2 \text{ eV}$).

Another experiment was carried out by depositing silicon oxide with 30 at.% concentration of oxygen [2-80]. Upon optimum annealing treatment at 400°C in vacuum, a highly connected nanosilicon network embedded in SiO_2 and doped with Er was obtained. An enhancement of room temperature PL intensity of Er as compared to that of crystalline Si doped with small oxygen concentration and Er was indeed observed. This is attributed to the photo-carriers being generated and trapped in the Er related defects and transferred to Er. There is no quenching of Er emission at room temperature because increase of bandgap of energy to about 2 eV caused energy backtransfer to be ineffective. Light emitting devices based on Er and oxygen doped Si has also been demonstrated [2-

80]. The emission is originated from impact excitation of Er, which results in the overall Er sensitization efficiency well below 100%.

2.2.2.2 Si-nanostructures as Er sensitizer

The room temperature Er emission in Er and O co-doped Si is attributed to the quenching of backtransfer process from Er to Er related defects due to the increase of host bandgap from 1.1 eV (Si) to higher energy. In addition, the improvement of Er environment from defective Si-rich oxide to higher oxidation also improves efficiency of Er emission [2-78]-[2-81].

Increase of the bandgap of the host matrix provides a much needed quenching of energy backtransfer for efficient Er emission at room temperature. One of the first demonstrations of the enhancement of Er absorption cross section by the presence of Si nanocrystals was reported by Fujii et al. [2-82]. Compared to the Er and O co-doped Si system, the Si nanocrystals are randomly dispersed in the matrix with spatial distance between nanocrystals in the 2-5 nm range, spherical in size, single crystalline although random in orientation, and dependent on the density of excess Si in the as-deposited samples [2-78]-[2-82].

Figure 2.9 The schematic of energy transfer (ET) from Si nanocrystals to Er^{3+} ions [2-74]

Figure 2.9 shows the schematic of energy transfer from Si nanocrystals to Er^{3+} ions embedded in SiO_2 matrix [2-74]. Upon excitation, usually ranging from 300nm to 500nm, a photon is absorbed by a Si-nanocrystal, causing generation of an exciton bound in the nanocrystal. If an Er ion is very near to the Si-nanocrystal, the exciton can recombine non-radiatively and excite Er into one of its excited states [2-82], [2-84], [2-85].

On the other hand, many works reported that amorphous Si nanostructures (Si nanoclusters) were also efficient sensitizer for Er emission [2-87]-[2-91]. With absorption cross section at visible wavelength four orders of magnitude higher than direct absorption cross section of Er (980 nm, or

$^4I_{15/2} \rightarrow ^4I_{11/2}$), the amorphous Si nanostructures indeed promises potential future for achieving efficient Er emission amplification. The working principle of carrier-mediated excitation of Er by amorphous Si-nanostructures is similar with that in the case of Si nanocrystals sensitized Er. The radiative rate of emission of amorphous Si nanostructures is lower than that of Si nanocrystals. In other words, the radiative lifetime of excitons generated in Si nanoclusters is much longer than that of Si nanocrystals, thus making efficient energy transfer rates to nearby Er ions possible. Si nanoclusters are generally formed by annealing Si-rich oxide (SRO) in inert ambient (Ar, and N₂) at temperature lower than 1000°C in prolonged period.

The sensitizing mechanism of Er by Si nanocrystals is strongly distance dependent. Ji-Hong Jhe et al. [2-92] reported that the exponentially decaying carrier-Er interaction has a characteristic interaction distance of 0.5 nm. Works reporting similar results of characteristics interaction distance in the range of 0.4-1 nm have also been reported in the literatures [2-94]-[2-96]. This means that for effective energy transfer, Er ions must be located not more than one or two atomic distance from the Si-nanostructures.

Since the energy transfer is strongly distance dependent, there is only a fraction of Er ions (in the range of 1% or lower) that is excited by the Si nanostructures [2-93],[2-94]. This suggests the necessity to produce a higher density of Er sensitizers, involving a system containing Si nanostructures as small as possible. Several authors have demonstrated that the Er related luminescence is a decreasing function of Si nanostructure size [2-95]. However, the size effect of Si nanostructures on Er emission is still not very clear. Several size-related properties of nanostructures, such as absorption cross section and also lifetime can be used to explain the abovementioned size-dependence energy transfer rate to Er. Watanabe et al. [2-95] suggested based on the time-resolved photoluminescence experiment that the energy transfer rate was greater for smaller Si-nanostructures, whereas another study by Gourbilleau et al. [2-96] demonstrated that Si nanocrystals with size equal to 4 nm can be a more efficient sensitizer than Si nanostructures with diameter of 2 nm because of a higher absorption cross-section. In general, such conflicting results demand further investigation so that a clear relationship between density and size of Si nanocrystals and energy transfer efficiency can be further clarified.

In most of the literatures, the Si nanostructures sensitized Er ions embedded in SiO₂ materials were usually fabricated by annealing of bulk Er doped Si-rich oxide (Er:SRO) thin films [2-74], [2-91], [2-97]. After annealing process at 1100°C, the large size distribution of Si nanocrystals makes the proper study on the size effect of the energy transfer to Er³⁺ ions difficult. For example, for Si-nanocrystals with wide range of size distribution, the energy transfer from smaller nanocrystals to larger nanocrystals is observed [2-98],[2-99]. To better understand the effect of Si nanostructures size on Er emission, an Er doped Si-rich oxide/SiO₂ (Er:SRO/SiO₂) superlattice structure would be a more

suitable approach due to the possibility of controlling the size of Si nanostructures. In this project, the author developed Er:SRO/SiO₂ superlattice samples and this will be discussed in Chapter 6.

2.3 Photonic Devices

The light efficiencies of Si nanostructures and Si nanostructures sensitized Er system are still low to compete with III-V materials for practical purpose. Nevertheless, several works on devices utilizing the Si nanostructures has been reported, such as Erbium doped waveguide amplifiers (EDWAs), electroluminescence devices, as well as photonic crystal (PC) structures. In this section, these three different devices are discussed.

2.3.1 Erbium doped waveguide amplifier (EDWA)

Si nanostructures, in crystalline or amorphous phase, are efficient sensitizer for Erbium (Er). With absorption cross section at visible wavelength four orders of magnitude higher than direct absorption cross section of Er (980 nm, or $^4I_{15/2} \rightarrow ^4I_{11/2}$), the Si nanostructures technology indeed promises potential future for achieving efficient Er amplification devices. One structure that has been widely investigated is the Erbium doped waveguide amplifier (EDWA) which is essentially a waveguide structure with amplification throughout the Er emission band centered at 1.55 μm .

Figure 2.10 (a) the cross section view of Er doped waveguide amplifier (EDWA) structure (b) The top optical pumping arrangement of EDWA structure [2-100], [2-101]

Figure 2.10(a) shows the cross section view of rib EDWA structure [2-100], [2-101]. The Erbium is doped in the guiding layer to optimize the spatial overlapping of fundamental mode and the Si nanostructures and Er ions. In Si nanostructures sensitized Er system, the requirement of optical

excitation wavelength may be relaxed due to large absorption cross section spectra of Si nanocrystals ($\sim 10^{-16} \text{ cm}^2$) [2-102]. The excitation wavelength does not have to be in resonant with $4f$ energy levels of Er, and visible excitation wavelength ranging from 300-500 nm can be used effectively for Si-nanostructure mediated energy transfer to Er. Furthermore, due to the much larger absorption cross section of Si nanostructures, low power sources, such as light emitting diode (LED) structures can be used in top optical pumping arrangement (see Figure 2.10(b)) in place of high power laser pumping co-propagating with the signal along the waveguide core.

Several interesting results on the EDWA structure using Si nanostructures sensitized Er have been reported by several authors [2-100],[2-101],[2-103]. However up to now, there is no net gain obtained from the EDWA devices. The low fraction of Er ions (1 % or lower) excitable by Si nanostructures, as well as the relatively high signal propagation loss of SiO_2 containing Si-nanostructures based waveguide are among several gain-limiting factors proposed by several authors [2-94], [2-100] Improvement of net gain per unit length is necessary to make the top optical pumping using light emitting diode (LED) an exciting option. If the length of waveguide is too long, e.g. few centimeters, the top pumping method is not possible because the waveguide layout area is too large to be covered by the LED quite uniformly.

2.3.2 Si nanostructure sensitized Er based electroluminescence

The electroluminescence (EL) of Si-nanostructure sensitized Er has been reported by several authors [2-106]-[2-108]. The EL spectra of Si-nanostructure or Si-nanostructure sensitized Er is in general obtained from metal-oxide-semiconductor (MOS) structures. There were varying results of EL characterization of Si-nanostructures and Si-nanostructure sensitized Er based MOS structures which were largely dependent on the sample preparation [2-106]-[2-108]. Until now, the reported EL spectra of Er were mainly originated from impact excitation mechanism and therefore raising the issue of device reliability [2-106],[2-109]. The difference in the PL and EL from Er-doped SiO_2 has been studied for different density of silicon clusters [2-108]. The sensitization from silicon clusters dominates the PL excitation of Er^{3+} , while impact excitation play important role in the EL excitation. When the average distance of the silicon clusters become less than the mean free path of the electrons in SiO_2 , direct tunneling of electrons and the average energy of hot electrons decreases, thus leading to a quenching of the EL from Er^{3+} [2-106]. The most notable work on the EL spectra of Si-nanostructures-sensitized Er in SiO_2 matrix was reported by Iacona et al. [2-108]. They highlighted that the amorphous Si nanostructures has more potential for electrically injected luminescent devices than Si nanocrystals. In amorphous Si nanostructures, the Si nanostructures are somewhat interconnected to each other, thus reducing the electrical barrier for the injected electrons.

2.3.3 Photonic crystal slab

In recent years, photonic crystal slab structure has been developed to enhance light extraction efficiency from light emitting diode structures, especially for III-V materials [2-110]-[2-114]. These materials are well known to have high internal quantum efficiency due to their direct bandgap properties. However, in the case of III-V material based light emitting diode, the extracted light output efficiency, i.e. the external quantum efficiency, is very poor, much due to the large difference in refractive indices of III-V materials (2.5-3) and air (1). Previously, to enhance light extraction, various methods such as, metal reflection layer [2-115], omnidirectional reflector [2-116], textured surface [2-117]-[2-119] and triangular chip [2-166] design have been investigated. All these approaches however only rely on the clever geometrical approaches to optimize the light output from the emitting material.

Another method that has been attempted is to increase the LED efficiency by direct modification of the spontaneous emission. First of this kind is reported by Schubert et al. [2-120] who demonstrated Fabry-Perot (FP) type microcavity. However, this approach only produce enhancement on certain resonant wavelength spectrum. Fan et al. [2-121] proposed an alternative approach of using photonic crystal slab structure to modify the spontaneous emission which can lead to enhancement over wide range of wavelengths.

Figure 2.11 Scanning Electron Microscopy (SEM) image of air hole triangular lattice photonic crystal slab structure reported [2-122]

The photonic crystal slab structure consists of a two-dimensional (2D) photonic crystal (core) with certain thickness (h) and surrounded by two layers of lower effective refractive indices, which are substrate (bottom) and upper cladding layer. Figure 2.11 shows the Scanning Electron Microscopy (SEM) image of air hole triangular lattice photonic crystal structure [2-122]. The lattice constant, which is the distance between two air hole centers, and radius of air-hole is labelled as a and r , respectively, in Figure 2.11.

Two different arrangements of photonic crystal structure for light enhancement has been experimentally demonstrated (a) separated from the emitting layer [2-111]-[2-114],[2-123] and (b) penetrating the emitting layer [2-122]. The first approach is suitable for III-V material based emitting layer because the crystalline quality of the sample is preserved. On the other hand, the second approach could be suitable for those amorphous materials which contain emitting centres, such as SiO₂ matrix containing Si-nanocrystals, because no requirement of good crystalline structure is required on the host matrix (SiO₂). In general, both approaches results in enhancement compared to the simple thin film without photonic crystal pattern. However, the penetrating structure could also produce an enhancement as well as modification of spontaneous emission more effectively than separated structure (first approach) [2-122].

Several parameters of photonic crystal slab structure such as refractive index of emitting medium, the hole size, the lattice constant, and the slab thickness are important parameters that need to be optimized to produce higher enhancement. This method is still recent and if the light enhancement has been well demonstrated, the electrically injected structure would be the next step.

In this project, the author chose to study the light enhancement in the visible (Si-nanocrystal related emission) and infrared (Si-nanostructures sensitized Er emission) spectra. Interesting phenomena of light enhancement and absorption modification will be discussed in Chapter 7.

2.4 Deposition methods

There are various kinds of techniques that have been studied to fabricate Si nanostructures embedded in SiO₂, such as ion implantation [2-124]-[2-129], chemical vapour deposition (CVD) [2-130]-[2-133], evaporation [2-134]-[2-138], co-sputtering [2-139]-[2-143], and also laser ablation [2-144],[2-145]. In general the silicon nanocrystals were formed by phase separation of excess Si in SiO₂ matrix at high temperatures. In this section, various kinds of relevant deposition techniques for developing Si-rich oxide (SRO) and Er:Si-rich oxide (Er:SRO) are discussed. The advantages and disadvantages of each method on the deposition of SRO and Er:SRO samples are presented. In this project, instead of bulk SRO and Er:SRO samples, the SRO/SiO₂ and Er:SRO/SiO₂ superlattice structures were developed and therefore the deposition method chosen must be suitable for depositing such structures.

Figure 2.12 The cross section view of SRO/SiO₂ or Er:SRO/SiO₂ superlattice structures developed in this work.

2.4.1 Implantation

Implantation technique is one of the first techniques used for formation of Si nanocrystals [2-124]-[2-129]. The excess Si concentration in host matrix is usually achieved by implanting Si⁺ ions. Implantations of Si⁺ and Er³⁺ are carried out at high energies, in the range of keV and MeV, respectively. The concentrations of excess Si and Er are determined by the implantation doses.

Incorporation of Er doped Si nanocrystals-containing SiO₂ film can be realized by two methods as follows: (i) Er doping after formation of Si nanocrystals in SiO₂ matrix [2-146]-[2-148], and (ii) co-implantation of Er and Si followed by annealing to obtain phase separation [2-91]. In the first method, the annealing process at temperature of 1100°C to form Si nanocrystals is carried out prior to incorporation of Erbium, thus avoiding the possibility of Er clustering at temperature higher than 900°C [2-91]. On the other hand, the work using second method has rarely been reported. This is possibly due to the difficulty in the annealing treatment to produce good Si nanostructures as well as curing defects to produce effective non-radiative energy transfer from Si nanocrystals to Er. PL spectra of Si-nanocrystals are also dependent on the thermal annealing effect. Prolonged thermal annealing at high temperature is definitely required to anneal out defects due to implantation damage and to produce Si nanocrystals. Thus, Si nanostructures and Si nanostructures-sensitized-Er fabricated by implantation method may not be effectively formed by low thermal budget.

Nevertheless, despite the possibility of incorporation of Er and Si nanocrystals in SiO₂ matrix, flexibility of the implantation method is quite limited and it is not suitable for realizing a uniform distribution of Er and Si nanocrystals. Furthermore, to develop more interesting structures such as SRO/SiO₂ and Er:SRO/SiO₂ superlattice, the implantation technique cannot be used. It is not possible to control the Si and O atoms implantation depth and profile to achieve alternating Si-rich oxide and SiO₂ layers. Above all, the implantation method is relatively more costly compared to other methods.

With all these abovementioned limitations, the implantation method is considered less suitable for depositing superlattice structures in this work.

2.4.2 Chemical Vapour Deposition (CVD)

Chemical Vapor Deposition (CVD) is one of the deposition methods of thin films by chemical reaction of gas precursors inside a reactor chamber. The useful product of the chemical reaction is in vapor phase which condenses into solid film on the substrate. Two most important CVD technologies are Low Pressure Chemical Vapor Deposition (LPCVD) and Plasma Enhanced Chemical Vapor Deposition (PECVD). In LPCVD technique, the films are deposited at high temperature ($>600^{\circ}\text{C}$) with low deposition rates. On the other hand, PECVD operates at relatively lower temperature ($\sim 300^{\circ}\text{C}$). PECVD is a modified version and industry proven technique and therefore compatible with complementary metal oxide semiconductor process used in the microelectronics industry.

Several development works on bulk Si-rich oxide (SRO) using PECVD technique [2-130]-[2-133], [2-149], [2-150], [2-151] and LPCVD [2-151],[2-152] have been reported. Although Morales et al. [2-152] reported that, after annealing treatment, samples deposited by LPCVD had better PL intensity than that of PECVD deposited samples, PECVD technique is much more extensively used to deposit Si-rich oxide (SRO) films because it is compatible with complementary metal oxide semiconductor (CMOS) process and it also produces a good control of Si content and film thickness uniformity, good adhesion to substrate, low deposition defects, and low compressive stress in the deposited films.

In PECVD, the sources used are mainly high purity silane (SiH_4) and nitrous oxide (N_2O). Different Si contents are achieved by variations of $\text{N}_2\text{O}/\text{SiH}_4$ flow ratio [2-149]-[2-151]. The use of N_2O , however, results in amorphous matrix containing nitrogen (N) atoms which could be as large as 10 at.% [2-150]. The incorporation of such a large concentration of N atoms does not contribute significant problem for emission of Si nanocrystals but it has been reported to be detrimental in the case of energy transfer from Si nanostructures to Er in the Er:SRO films [2-153]. The formation of silicon oxynitride on the surface of Si nanostructures has been reported by Heng et al. [2-153], which reduces the energy transfer rate to Er ions. In addition, the incorporation of Er using PECVD system also poses several problems, such as the need for Er in gaseous phase as well as the need for separate gas (precursor) line to avoid any severe contamination. Therefore, in general CVD method produces less efficient sensitizing effect of Si nanostructures on Er emission due to the presence of unavoidable Si oxynitride and also due to Er contamination introduced into the chamber. To the author's

knowledge, there has been no multilayer Er:SRO/SiO₂ superlattice structures developed using PECVD.

2.4.3. Physical Vapour Deposition

Two most popular Physical Vapour Deposition (PVD) methods used in the fabrication of Si nanocrystals are evaporation and co-sputter deposition techniques. These two methods will be discussed below.

2.4.3.1 Evaporation deposition technique

The evaporation technique is a physical vapour deposition method (PVD) to deposit films by evaporating the source which then condenses and form a solid film on the substrate. The atoms evaporated from the source to the substrate follows straight line path. In general, to deposit SRO layers, the SiO and Er:SiO powder, respectively, are evaporated [2-134]-[2-138]. During the film deposition, oxygen with partial pressures ranging from 10^{-3} to 10^{-4} Pa, is used to control the concentration of excess Si in oxide matrix. The deposition rates of the films are usually high, thus posing difficulties in controlling the thickness of SRO layers in the SRO/SiO₂ superlattice structures, as indicated in Figure 2.9. Nevertheless, the work on reactively evaporated SiO/SiO₂ superlattice samples has been reported by Zacharias et al. [2-53]. In addition, Heitmann et al. [2-154] reported the work on Er:SRO/SiO₂ superlattice layers using Er implantation of reactively evaporated Er:SRO/SiO₂ superlattice structure. This might be due to the difficulty in controlling small concentration of Er in SRO layers due to the high deposition rates of evaporation technique.

2.4.3.2 Co-sputter deposition technique

The sputter deposition technique is a physical vapour deposition (PVD) method of depositing films by sputtering or ejecting the material from the target material (source), which then condenses and form solid films on the substrate. The sputtering of the source target requires positive ions which are induced by radio frequency (RF) field [2-155]. Sputtering target sources are usually mounted on the target holder equipped with magnetrons which utilize strong electric and magnetic fields to trap electrons close to the surface of the target. The electrons follow helical paths around the magnetic field lines undergoing more ionizing collision with gaseous neutrals near the surface of the target. The positive ions which are responsible for sputtering the target are generated through this ionizing collision [1-155]. The ionizing collision creates accumulation of large positive ions inside the plasma

and the target surface which is usually negatively charged results in a dark space shield. This dark space is responsible for acceleration of positive ions to sputter or eject the atoms on the target surface. Furthermore, reactive oxygen involving other additional reactive gases, such as O_2 and N_2 , can also be used to provide the required stoichiometry of the films. For examples, in depositing SiON films, which will be discussed in more detail in Chapter 8, the Ar, N_2 and O_2 gasses are used and the chemical compositions of the SiON films are controlled by controlling the partials vapour pressure of N_2 and O_2 gases.

The most important advantage of sputter deposition method is that it is a relatively simple technique and can be used to deposit any materials, ranging from oxides [2-139]-[2-143], [2-156], [2-157], metals [2-158]-[2-160] to multicomponent materials [2-161],[2-162]. Materials with high melting temperatures which are not easily evaporated can be easily sputtered. In general, the deposited materials have composition similar to the source material, especially at low deposition rates. If incorporation of multiple elements in the deposited films is desired, the co-sputtering of multiple targets, generally known as the co-sputtering technique, is carried out.

The development of Si-rich oxide (SRO) and Er-doped Si-rich oxides (Er:SRO) by sputter deposition technique have been extensively reported in the literatures. Basically, the incorporation of excess Si can be realized with relative ease by using several methods: (i) using Si and SiO_2 targets [2-163] and (ii) reactive sputtering of SiO_2 target using sputtering gas mixture of Argon (Ar) and Hydrogen (H) [2-164]. The incorporation of Er can be done by simply adding Er_2O_3 target [2-165] or by placing Er pellets on top of the surface of SiO_2 target [2-166].

In this project, the author concluded that co-sputter deposition of Si, SiO_2 , and Er_2O_3 targets to be a suitable method to deposit SRO/ SiO_2 and Er:SRO/ SiO_2 superlattice structure on planar substrate due to the following reasons:

1. The co-sputtering technique offers flexibility to deposit multicomponent materials, such as Si-rich oxide and Er:Si-rich oxides layer.
2. The deposition rates of sputtering method are low, which offers relative ease for controlling the thickness of SRO and SiO_2 layers in nanometer scale, as well as concentration of Er.
3. The co-sputter deposition technique to form Er doped SRO layers offers low cost approach as compared to Er implantation.
4. The co-sputtering technique allows independent control of each target and therefore enables the incorporation of Er in any layer desired.

In this thesis, the development of SRO/ SiO_2 and Er:SRO/ SiO_2 superlattice structures using the co-sputtering technique will be discussed in Chapter 4 and Chapter 6, respectively.

2.4.4 Thermal Annealing Process

In all works reported in this literature review, the formation of Si nanostructures was induced by thermal annealing of the excess Si containing SiO_2 materials. This annealing treatment to produce nanocrystals by phase separation of Si-rich oxide into Si nanoclusters and SiO_2 phase is usually carried out at high temperatures ($\sim 1100^\circ\text{C}$) in the pure inert ambient such as Ar and N_2 or in vacuum for relatively long time (~ 1 hour). This was necessary to avoid the presence of relatively high residual oxygen gas in which otherwise resulted in a more dominant oxidation mechanism rather clustering of excess Si. The high purity of inert gas or high level vacuum is required for annealing.

Figure 2.13 Formation of Si-nanocrystals in SiO_2 matrix [2-51]

Figure 2.13 shows the formation of Si-nanocrystals in SiO_2 matrix [2-51]. Long annealing at high temperature ($\sim 1100^\circ\text{C}$) is necessary for effective clustering of the excess Si atoms. A prolonged time is also necessary to further nucleate and crystallize the nanostructure and lastly improve the interface quality of Si nanocrystals and surrounding silica matrix. As the annealing time increases, smaller Si clusters disappear while larger Si nanocrystals increase in size. In Figure 2.13, it is also shown that instead of perfectly embedded in SiO_2 which has energy barrier of ~ 9 eV, Si nanocrystal was encapsulated by a stressed SiO_x ($x < 2$) shell, which separates the Si nanocrystal and surrounding SiO_2 matrix [2-51].

The photoluminescence (PL) of Si nanocrystals embedded in SiO_2 in general consists of two PL bands: defect-related PL bands, at 400-500 nm, and Si nanocrystals related PL bands, ranging from 700 extending to ~ 1000 nm [2-128], [2-131]. As indicated in the Figure 2.13, the clustering process is somewhat a random process with a strongly dispersive size of Si nanocrystals. This is marked by a broad Si nanocrystal related PL bands at 700-1000 nm. It is also generally observed that the emission of Si nanocrystals in SiO_2 is located at longer wavelength than that of Si nanocrystals

with similar size in porous Si system, which is shown in Figure 2.3 above. The apparent PL peak shift of Si nanocrystals in SiO₂ can be qualitatively explained using model proposed by Wolkin et al. [2-39], which attributed such PL peak shift to the presence of Si=O bonds on the surface of Si-nanocrystals.

Several authors have also reported the study on the annealing time on the properties of Si nanocrystals embedded in SiO₂. They reported that the average size of Si nanocrystals was determined during the first few minutes of annealing in inert atmospheres [2-152], [2-167], [2-168]. At longer annealing time, the passivation of Si nanocrystals/SiO₂ interface is more dominant, evidenced by the increase of PL peak intensity with only slight shift of PL peak wavelength with longer annealing time. Such long annealing process imposes a high thermal budget requirement. As an alternative to a prolonged annealing in high temperature, a combination of short annealing at high temperature (1100°C) in inert ambient (N₂, or Ar) to form the Si nanostructure and passivation of defects by annealing in forming gas (H₂:N₂) has also been reported [2-168]. When the Si nanostructures are formed, the remaining defects are cured by hydrogen passivation by annealing in forming gas (N₂:H₂) at lower temperature (400-600°C) for 1 hour. Furthermore, in the case of Er doped Si-rich oxide, the optimum Er emission intensity was obtained after annealing at 850°C in N₂ for 1 hour, which was below the onset temperature for Si crystallization (1000°C). This implies that crystalline Si nanostructure, i.e. Si nanocrystal, is not required as efficient Er ions sensitizer.

The use of rapid thermal annealing (RTA) has not been properly explored for the formation of Si nanostructures. Principally, because the clustering of Si atoms to a considerable size of few nanometers begin to occur at temperatures of only 800°C [2-169] a short annealing (in few minutes) at slightly higher temperatures in inert gas should be able to produce Si nanostructures. Using RTA at temperatures slightly higher than 900°C in inert atmospheres (Ar N₂), it could be possible to avoid the possibility of precipitation of Er due to inhibition of diffusion of Er ions which is very low even at high temperature [2-169].

Another interesting rapid annealing method to be investigated is Excimer laser annealing (ELA) method. The excimer laser annealing has been widely used to anneal doped samples at very short time to avoid large diffusion of dopants [2-170],[2-171]. The excimer laser system which was usually utilized is KrF excimer laser system operating at 248 nm. The advantage of ELA process is the ability to generate localized heating treatment. This is suitable for substrates with low temperature stability. These two annealing methods (RTA and ELA processes) were applied in this work and they will be presented and discussed in Chapter 4.

2.5 Summary

The author has reviewed the theory and development works on the Silicon (Si) nanostructures related emission in the visible wavelength (700-900 nm), from the porous Si to Si nanocrystals embedded in SiO₂ material. In this Chapter, the author has also reviewed the reported studies on the sensitizing effect of Si nanostructures on Er-related emission at optical communication wavelength, 1.55 μm . The Photoluminescence (PL) peak wavelength of Si-nanostructures can be tuned by varying the average size of Si nanostructures. Instead of varying the excess Si concentration which is quite random and heavily process dependent, the Si-rich oxide/SiO₂ (SRO/SiO₂) superlattice structure was found to offer possibility to control the Si nanostructure size and PL peak wavelength. Furthermore, using this superlattice structure, the study on the Si nanostructure size dependence of energy transfer to Er can also be carried out. The author also reviewed the various deposition techniques used in fabricating the Si-nanostructures embedded in SiO₂ as well as Er doped Si-nanostructures in SiO₂. The selection of deposition method used in this project is based on the two considerations, which are (i) the possibility of depositing good SRO/SiO₂ and Er:SRO/SiO₂ superlattice samples with low cost, and (ii) the possibility of controlling the position of Er ions in the structure. The author has also observed that high budget thermal annealing process (high annealing temperature and long annealing time) has been commonly used to produce Si-nanostructures in SiO₂ matrix. In this project, the author has focused on the development of low thermal budget annealing, such as the rapid thermal annealing (RTA) and excimer laser annealing (ELA) processes to produce Si nanostructures and Er related PL emissions. Lastly, a brief review on several photonics devices has also been presented. An interesting and new approach of implementing photonic crystal structure on emitting layer (Si nanostructures or Er:Si nanostructures containing SiO₂ material) has been chosen to improve the Si nanostructures and Er related PL emission intensities.

Chapter 3

Characterization Techniques

3.1 Introduction

In this chapter, the author discusses various characterization techniques that were used in the development of Silicon-rich oxide/SiO₂ (SRO/SiO₂) and Erbium (Er) doped Silicon-rich oxide/SiO₂ (Er:SRO/SiO₂) superlattice samples, the SRO/SiO₂ and Er:SRO/SiO₂ superlattice based photonic crystal (PC) slab structures, as well as the silicon oxynitride (SiON) thin films and slab waveguides. In section 3.2, the author describes the thin film characterization techniques used to study the optical and physical properties of the superlattice samples. In section 3.3, various imaging techniques will be described. In section 3.4, the characterization techniques of the photonic crystal slab structures developed based on the superlattice samples will also be described.

3.2 Thin film characterization techniques

The characterization techniques are necessary to provide the knowledge of optical, structural, as well as physical properties of the treated SRO/SiO₂ and Er:SRO/SiO₂ superlattice samples. Various kinds of material properties obtained were refractive index, photoluminescence spectra, microstructure properties, infrared absorption properties, and atomic composition and characterization of slab waveguide of the developed samples

3.2.1 Thin film characterization techniques: spectroscopy techniques

Various spectroscopy techniques such as UV-Visible spectroscopy, Fourier transform infrared (FTIR), spectroscopic ellipsometry (SE), and photoluminescence (PL) spectroscopy were used in this work and will be discussed below.

3.2.1.1 UV-Visible spectroscopy

The transmission spectroscopy is involved in many analytical works on optical materials [3-1]-[3-3]. In this work, the UV-Visible spectroscopy is utilized to observe the transparency of the SiO₂

and Si-rich oxide (SRO) layers. The reported absorption spectra of the samples were measured by Hewlett Packard model HP8453 UV-Vis spectrometer. The scanning wavelength range is from 190-900 nm, with a resolution of 1 nm. The measured sample has to be transparent and therefore, in practice, the substrate used must have high transparency over the UV to visible wavelength spectrum. In this project, the author used high quality UV-grade fused Silica plate Corning 7980 glass as the substrates, which are highly transparent from infrared (IR) to UV regions of ($\lambda < 190$ nm).

Figure 3.1 Block diagram of UV-Vis spectrometer [3-4]

The block diagram of UV-Vis spectrometer is shown in Figure 3.1 [3-4]. The light source consists of a deuterium discharge lamp to generate ultraviolet (UV) light and a tungsten-halogen lamp to produce visible and near infrared (NIR) spectra. The instrument automatically switches from the former deuterium to tungsten-halogen lamp as it scans from UV to visible regions. One of the problems in the transmission measurement is the stray light which is defined as the detected light of any wavelength outside the bandwidth of the selected wavelength. The stray light problem is more severe for high absorbance measurement in the Ultraviolet (UV) region. Therefore, the design of spectrometer and its optical components is optimized to reject this stray light.

3.2.1.2 FTIR spectroscopy

Infrared (IR) spectroscopy is a powerful tool to study the atomic bonds present in the materials, irrespective of crystalline or amorphous nature [3-5]-[3-7]. This technique is also extensively used to study the structural sites occupied by O-H and N-H bonds in various materials, such as Silicon oxynitride [3-8]. In this work, the use of the IR spectroscopy is to determine different chemical functional groups in the developed superlattice samples (in Chapter 6) and silicon oxynitride (SiON) samples (Chapter 8).

Figure 3.2 Schematic diagram of FTIR spectrometer [3-9]

Fourier transform infrared spectroscopy (FTIR) collects all frequencies (wavenumber) simultaneously, leading to a high speed measurement [3-9]. In addition, FTIR also has a better sensitivity. The working principle of FTIR system is typically based on Michelson Interferometer [3-9], as shown in Figure 3.2. The interferometer consists of a beam splitter, a fixed mirror, and high precision movable mirror (front and back). The beam splitter splits the incident infrared (IR) radiation into two beams: transmitted beam travelling to the movable mirror and reflected beam travels to the fixed mirror. These two beams are then reflected back from the two mirrors to the beam splitter, resulting with one beam travelling to the sample and detector. The signal recorded by detector is referred to as interferogram, i.e. plot of light intensity versus moving mirror position. This information is to be translated into an absorption spectrum, i.e. plot of intensity versus wavenumber, to identify the molecular vibrations by a mathematical process of Fourier transformation in the computer/controller section.

FTIR spectra reported in this thesis were carried out between $2.5\ \mu\text{m}$ to $25\ \mu\text{m}$ ($4000\ \text{cm}^{-1}$ to $400\ \text{cm}^{-1}$) with a $2\ \text{cm}^{-1}$ resolution by Perkin-Elmer Spectrum 2000 spectrometer in absorption mode. This range of wavenumbers (in cm^{-1} unit) includes all the absorption frequency of the majority of the molecular vibrations in the samples. Samples used for FTIR characterization was deposited on a high-resistivity Si wafer ($\sim 10\ \Omega\ \text{cm}$). A high resistivity Si substrate was needed to avoid large IR absorption due to free carriers so that the IR absorption spectra data obtained was reliable. Prior to the FTIR measurement, a bare Si wafer from the same batch of Si substrates was used to measure the background signal.

3.2.1.3 Spectroscopic ellipsometry

Spectroscopy Ellipsometry (SE) is the method used to derive the optical constant of material: refractive index (n), extinction coefficient (k) and film thickness to a high degree of precision [3-10]. This measurement technique has a high accuracy due to the fact that it is based on the measurement of polarization change which is not affected by any spurious ambient phenomenon. This is unlike the case of reflectance or transmittance measurements which are often prone to other ambient light or even source drift. This technique measures the change in the state of polarization of light upon reflection from the sample surface and determines the ellipsometric parameters ψ and Δ . These values are related to the ratio (ρ) of Fresnel reflection coefficient of p-polarized waves (r_p) and s-polarized waves (r_s), through the following equations:

$$\rho = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan \Psi e^{i\Delta} \quad (3.1)$$

The Spectroscopic ellipsometer (SE) used in this work was the J.A. Woollam Company VASE spectroscopic ellipsometer. The experimental set up of SE is shown in Figure 3.3(a) [3-10] below. The light coming out from light source is polarized and then incident to a sample. The reflected light is then transmitted through and analyzer and detected by detector. This detector records the rotation angles of the polarizer and analyzer enables the determination of the phase difference (Δ) and amplitude ration ($\tan \psi$) of the s- and p- components of the reflected light. In Figure 3.3(b), the interaction of polarized light with the sample is shown. A linearly polarized input beam is converted to an elliptically polarized reflected beam.

(a)

(b)

(c)

Figure 3.3 (a) Typical set up for spectroscopic ellipsometry measurement and (b) interaction of light with the sample [3-10], (c) an example of fitting of experimental data for a SiON film sample, with the inset showing a derived spectral profile of refractive index profile (n) and extinction coefficient (k) of SiON film in Chapter 8

The ellipsometric parameters, ψ and Δ were obtained using the rotating analyzer. All measurements were done at room temperature with an angle of incidence at 75° (with respect to normal line) and in the wavelength range from 270 to 1700 nm. Since the ellipsometer only provides the variation of parameters ψ and Δ over wavelength spectrum, a proper modeling and fitting was necessary in order to derive the correct refractive index (n), extinction coefficient (k) as well as thickness of the samples. The spectral data of ψ and Δ were fitted to the material properties described

by oscillator models, such as Tauc-Lorentz oscillator models, as well as the thickness and uniformity of the layer. To obtain the fitting parameters, the Levenberg-Marquardt regression method, built in the VWASE32 software provided by J.A. Woollam, Inc [3-10] was used. In this work, SE technique was used to obtain the refractive index of SiO₂ layer used in the SRO/SiO₂ superlattice samples and SiON samples. To confirm the fitting results, an independent measurement of sample thickness was done using surface profilometry, which will be explained in Section 3.2.2.4. In Figure 3.3(c), an example of fitting of experimental data of a SiON sample, which results in spectra profile of refractive index (n) and extinction coefficient (k) in the inset, is shown.

3.2.1.4 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is one of the widely used characterization techniques for developing luminescent materials [3-11]-[3-13]. Upon optical excitation, the photoemission from the sample under test is detected over wavelength spectrum. In this work, the photoluminescence spectra of Si-nanostructures and Er ions and photonic crystal (PC) slab structures were obtained by the Fluorolog-3, IR PL set-up, and Micro-Raman PL spectroscopy, respectively. These three different PL arrangements will be described below.

3.2.1.4.1 Fluorolog-3 photospectrometer

Fluorolog-3 (FL3-11) spectrometer was used to measure the Photoluminescence of the treated SRO/SiO₂ samples in the visible to near infrared (NIR) wavelength spectrum, ranging from 350 to 900 nm. The schematic diagram of FL3-11 spectrometer was shown in Figure 3.4 [3-14]. The excitation source is Xenon lamp with a broadband spectrum, ranging from 250 to 2000 nm. The excitation and emission monochromators work in the range of 200 to 950 nm. The photomultiplier tube (PMT) having a spectrum from 250 to 900 nm to detect the emitted light from the sample.

Figure 3.4 Schematic diagram of FL3-11 spectrophotometer [3-14]

Each of excitation and emission spectrometer has single-grating arrangement. A thin film sample was placed at the sample holder located in the sample compartment module. Prior to the sample measurement, the excitation monochromator and emission grating are calibrated by scanning the broadband Xenon lamp source (200-2000 nm) and by measuring water emission spectrum, respectively. The excitation calibration should ensure that the Xenon lamp source has a peak at 467 ± 0.5 nm whereas the emission should be calibrated by water Raman spectral peak at 398 ± 0.5 nm. The resolution of the measurement is 1 nm. The excitation wavelength can be selectively chosen by the use of monochromator. When scanning the emission spectrum, the second harmonic region related to the excitation wavelength has to be avoided to prevent overloading of the photomultiplier tube (PMT). This is the reason that the visible PL spectrum of the samples at certain region of wavelength, depending on the excitation wavelength used, is truncated as large as ~ 40 nm.

3.2.1.4.2 Photoluminescence (PL) for Infrared (IR) system

To measure the Erbium (Er) emission at $1.55 \mu\text{m}$, the author used a photoluminescence (PL) set up capable of measuring the photoluminescence in the infrared (IR) spectrum. The infrared (IR) PL set up consists of several important components, namely: the optical excitation using laser source, the optical instruments consisting of mirrors, lens, and objectives lens, slit, and reflectors.

Figure 3.5 Schematic of Infrared (IR) photoluminescence (PL) set up used to measure photoluminescence of Erbium.

The optical excitation was performed using He-Cd laser at wavelength of 442 nm with a nominal power of 40 mW. This particular wavelength is non-resonant to any energy levels in Er ion; a requirement to ensure the Er-emission is related to sensitizing effect of Si nanostructures [3-15]. The Er-doped sample was irradiated by focussed excitation beam with diameter of ~ 1 mm on the surface of the measured sample and the scattered emitted light was collected and collimated by an arrangement of optical lens to the InGaAs photodetector. The lock-in amplifier was matched to the chopper frequency of 172 Hz to avoid interference with ambient light frequency, which is usually at 50 Hz. The InGaAs photo-detector is used to measure the Er-related PL from 1450 to 1650 nm. The resolution of the measured PL spectra is 1 nm. All measurements were carried out at room temperature.

3.2.1.4.3 Micro-Raman photoluminescence system

The Micro-Raman photoluminescence (PL) system is important for the PL measurement of a multiple pattern/structure on a single substrate. [3-16], [3-17]. The PL characterization of SRO/SiO₂ and Er:SRO/SiO₂ superlattice based Photonic Crystal (PC) slab structure was carried out using a Micro-Raman PL system.

Figure 3.6 Schematic diagram of Micro Raman Photoluminescence (PL) system [3-18]

Figure 3.6 shows the components of micro-raman PL system [3-18]. Several important parts of the Micro-raman PL system are listed as follows: laser system operating at wavelength of 488 nm as the excitation source, photo-detectors working from visible to infrared spectrum (400-1600 nm), optical imaging system, and high precision XY micro-positioning stage. The micro-positioning stage enables precise placement of the detector on any location on the surface of the PC structure. The recorded PL intensity is measured from vertically directed emission of the structure. The excitation beam is focussed to a diameter of $\sim 3 \mu\text{m}$.

3.2.1.4.4 Lifetime measurement

To understand the nature of radiative emission of Si nanostructure, the knowledge of PL life time is also necessary [3-19], [3-20]. In a matrix containing Si-nanostructure, the nature of interaction between neighbouring nanostructures and nanostructures with nearby defect level can be obtained by fitting the related Photoluminescence lifetime with a stretched decay exponential function [3-21]:

$$I(t) = I_0 \exp\left(-\left(\frac{\tau}{t}\right)^\beta\right) \quad (3.2)$$

where I_0 , τ , and β are initial decay intensity, effective lifetime, and stretching parameter constant. When $0 < \beta < 1$, the neighbouring nanocrystals interact with each other. As β approaches 1, the nanocrystals are effectively separated from each other [3-20], [3-21].

In this work, two lifetime measurement systems were employed. The first system is the SPEX 1934D Phosphorimeter, which was used for measuring Si-nanostructure lifetime in the range of 10-100 μs . This system is part of the Fluorolog-3 Photospectrometer system discussed in the section 3.2.1.4.1 above. In this system, the emission line selected for lifetime measurement is fixed at 325 nm.

The second system is the Edinburgh Instrument FL92, which was used for measuring defects-related emission lifetime in the range of 1-10 ns. For the Edinburgh system, the excitation source is laser source with emission line at 371 nm. Nevertheless, although the laser wavelength is slightly different from that used in the first system, it is still capable of exciting the defects emission at 400-500 nm by using filter with sharp band pass edge.

3.2.2 Thin film characterization: structural techniques

In this section, the characterization techniques to determine the microstructure of the samples such as Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), X-ray photoelectron study (XPS) and Surface Profiler will be discussed below.

3.2.2.1 Transmission electron microscopy (TEM)

The transmission electron microscopy (TEM) technique is a useful technique to obtain structures within nanometer size in a sample [3-22], [3-23]. The basic principle of TEM is discussed below. Figure 3.7 shows the schematic diagram of TEM technique [3-24], which operates on the same basic principles as the light microscope but uses electrons instead of the light. TEM uses electrons as a “light source” because their much shorter wavelength enables a resolution a thousand times better than using light microscope.

Figure 3.7 Schematic diagram of Transmission Electron Microscopy (TEM) [3-24]

Chapter 3

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As shown in Figure 3.7, the electron beam travels down through the vacuum in the column of the microscope. The electrons are guided by electromagnetic lenses to focus the electrons into a very thin beam. The electrons then travel through the prepared specimen. Depending on the density of the material, some electrons are scattered and disappear. At the bottom of the microscope, the unscattered electrons hit a fluorescent screen giving rise to a shadow image of the specimen with its different parts displayed in varied darkness according to the density. A camera is used to capture the image.

In this work, TEM technique was used to obtain the presence of Si-nanocrystals and the superlattice arrangement in the silica matrix. The cross-section of the thin film samples was investigated. The specimens were cut in the thickness cross section area and thinned down mechanically before milled using Precision Ion Polishing System (PIPS).

In this work, because the size of nanostructure (crystalline or amorphous) is small, in the range of 2-6 nm, the mechanical preparation of the samples is crucial. During the thinning of the sample using PIPS treatment, the angle of ion beam was set a very small angle 2° to 5° to obtain good TEM samples. At larger angle of incident ion beam, the samples will be polished excessively, leaving a large hole in the centre of the sample, which damage the region of interest for TEM measurement.

3.2.2.2 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a quantitative technique used to measure the elemental composition on the surface of the materials [3-27], [3-28].

Figure 3.8 Interaction of x-ray beam and the material [3-29]

Figure 3.8 shows the incident x-ray beam focused on the surface of the sample which then generates the photo-emitted electrons beam [3-29]. Each element produces a characteristic set of XPS peak at characteristic binding energy values. These characteristic peaks correspond to the configuration of electrons in the atoms, for example 1s, 2s, 2p, 3p, etc. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element in the irradiated area (volume). The raw XPS signal has to be corrected by a relative sensitivity factor of the system and normalized throughout all of the elements detected. The ultra high vacuum (UHV) chamber is necessary because the detectors are relatively far (~1 meter) from the x-ray irradiated sample.

XPS technique detects only those electrons that have actually escaped into the vacuum of the instrument. The photo-emitted electrons that have escaped into the vacuum are those originated from within the top ~10 nm of the sample. In this project, the XPS technique was used to measure the concentration of atomic composition of Si and O in Si-rich oxide (SRO) layer. SRO layer having thickness of around 30 nm was used for XPS characterization.

3.2.2.3 Surface profiler

Surface profiler is a useful technique to provide information on thickness of the films. Thin film thickness was measured by electromechanically moving a diamond tipped stylus along a trench profile on the sample. Figure 3.9 below shows the schematic diagram of this technique [3-30]. Diamond-tipped stylus was mechanically coupled to LDVT (Linear Variable Differential

Transformer). The stylus rides over the sample in a particular direction. The thickness variation on the surface causes the stylus to be translated vertically and changes the core position of LDVT. This change of position will generate current that is corresponding to stylus movement along the surface. The accuracy of this method is affected by any vibration of the environment.

Figure 3.9 Block diagram of surface profiler [3-30]

In this work, Dektak profilometer was used to get the accurate film thickness. A step pattern, which was obtained by masking during deposition process, was obtained in the horizontal span of 500 μm .

3.3 Imaging Techniques

In this section, the author discusses imaging techniques, such as optical microscopy, and scanning electron microscopy which were used to characterize the samples.

3.3.1 Optical microscopy

In this work, NIKON optical microscope system was used for several purposes: to observe the surface quality of the prepared samples and to observe the quality of sample prepared for TEM characterization. In the latter, a good quality of ion-milled “crater” has to be observed by optical microscopy before the sample was loaded into TEM system, explained in section 3.2.2.1.

3.3.2 Scanning electron microscopy (SEM)

In this work, JEOL JSM-5600LV Scanning electron microscopy (SEM) was used to observe the image of the fabricated photonics crystal slab samples. The interaction of light and the sample surface is illustrated in Figure 3.10 [3-31] below.

Figure 3.10 Sample interaction with the electron beam [3-31]

The energetic electrons strike the sample and various reactions occur. Secondary electrons were detected by the detector and variations in intensity of these secondary electrons were translated to a difference contrast on the screen, creating an image of the surface topography of the sample.

3.4 Other characterization technique: prism coupler technique

In this section, the author describes the prism coupler technique, which was used to determine (i) the effective refractive index of SRO/SiO₂ superlattice layer, and (2) the refractive index and propagation loss of the SiON based slab waveguide. In the case of SRO/SiO₂ superlattice layer, the prism coupling method offers simplicity in determining the refractive index as compared to spectroscopic ellipsometry technique, which requires fitting using oscillator models.

3.4.1 Determination of refractive index and thickness

The prism coupler technique is used to characterize planar slab waveguide and derive several properties such as refractive index, thickness, as well as propagation loss [3-32]-[3-33]. This technique was used because of its inherent advantage of high coupling efficiency (up to 80% for a

Gaussian beam), applicability to the planar waveguides and selective excitation of any of the guided modes.

Figure 3.11 (a) Prism coupler arrangement, (b) the reflected beam intensity as a function of angle (θ) recorded by detector [3-36]

The measurement was performed by using the Metricon 2010 prism coupler as shown in Figure 3.11(a) [3-34]. The set up has two different wavelength sources: 632.8 nm and 1550 nm. For the samples in this work, a prism with refractive index of 2.4 (higher than the guiding layer index) was used in this measurement. The sample is mounted vertically on the prism coupling stage. The pressure applied against the base of the prism is carefully adjusted in order to improve the coupling efficiency. The precision rotation stage allows the variation in angle of incident beam. The accuracy of refractive index derived from this system is 0.0005 (for slab waveguides that support two or more modes). Figure 3.11(b) shows the typical recorded data plot of intensity versus angle of incidence. The dip observed corresponds to a mode coupling to the slab waveguide structure.

In this measurement, the measured layer needs to have refractive index higher than the substrate, thus forming a structure sandwiched between lower indices: substrate and air ($n=1$). This is necessary so that light can be guided along the layer of interest. The layer also needs to be thick enough to at least support a propagation mode, marked by the dip in Figure 3.11(b).

3.4.2 Loss measurement

Using the mode angle corresponding to the fundamental mode in the measured slab waveguide, propagation loss of the optical slab waveguides can be measured. The loss measurement was carried out by exciting at the fundamental mode angle while moving a fiber along the propagation line to collect the scattered light of the propagating mode. The propagating mode experiences decay in intensity, as described by the following equation:

$$I(x) = I_0 \exp(-\alpha x) \quad (3.3)$$

where α is the attenuation coefficient per unit length, I_0 is the initial power, and x is the distance, whereas $I(x)$ is the transmitted power through a waveguide a distance x .

3.5 Summary

In this chapter, the author presents various characterization techniques used to analyze and characterize the properties of the developed samples (SRO/SiO₂ and Er:SRO/SiO₂ superlattice thin films and Photonic crystal (PC) slab structure as well as the SiON thin films) presented in this thesis. The characterization techniques used in this work are divided into four categories as follows. The first category is spectroscopy techniques which consist of UV-Visible, FTIR, spectroscopic ellipsometry, and photoluminescence spectroscopy techniques. The second category is structural techniques, consisting of transmission electron microscopy, x-ray photoelectron spectroscopy and surface profiler. The third category, imaging techniques, consist of optical microscopy and scanning electron microscopy. Lastly, prism coupling technique which was used to determine refractive index, thickness and loss measurement of slab waveguide structures based on the samples developed here was also described.

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4.1 Introduction

As reviewed in chapter 2, the photoluminescence (PL) in visible to near-infrared (500-1000 nm) could be obtained by varying the average size of Silicon (Si) nanocrystals (Si-nc). The shrinkage of Si to nanoscale size (< 5 nm) results in room-temperature emission much more efficient than that of bulk Si because of the spatial confinement of excitons [4-1], [4-2]. The mechanism of this emission can be attributed to excitons through quantum confinement effect [4-3], [4-4] or surface states [4-5]-[4-6]. These mechanisms have been explained in chapter 2 section 2.2.1.

One common approach to form Si nanocrystals embedded in SiO₂ is by annealing process of bulk Si-rich oxide (SRO) structures. There are various deposition methods which can be used to introduce excess Si concentration, such as evaporation [4-7], [4-8], sputtering [4-9], [4-10], chemical vapour deposition (CVD) processes [4-11], [4-12], as well as implantation of Si into thermally grown SiO₂ films [4-13]. These deposition methods have been discussed in more detail in Chapter 2 section 2.4. Subsequently, post-deposition annealing at high temperatures (>1000°C) for relatively long period, e.g. 1 hour, is normally employed to induce phase separation of Si and SiO₂ followed by nucleation and crystallization of Si clusters [4-7]-[4-16]. However, this approach results in a large size distribution of Si nanocrystals in bulk Si rich oxide (SRO) structure leading to a broad PL peak (larger FWHM) upon excitation. It is also difficult to control the PL peak wavelength because, upon thermal annealing, the size of Si nanocrystals (Si-ncs) is largely dependent on the excess Si concentration. During the prolonged annealing time, the size of larger Si nanocrystals grows at the expense of smaller Si nanocrystals. Therefore, despite its simplicity, the bulk Si-rich oxide (SRO) approach poses a problem of controllability of PL peak wavelength and also large size distribution of Si nanocrystals.

Using a Si-rich oxide/SiO₂ (SRO/SiO₂) superlattice structure, the problem of Si nanocrystals size controllability in the SRO sample could be alleviated [4-14], [4-17]. Zacharias et al. [4-14] reported that using similar post-deposition annealing treatment on bulk SRO sample, the PL peak wavelength and the size distribution of superlattice samples were better controlled and narrower, respectively, than those of bulk SRO sample.

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In this chapter, the author presents the development work on the Si nanocrystals embedded in silica (SiO₂) material with PL peak wavelength controllability. SiO₂ was chosen as the host material due to several reasons explained earlier in chapter 2 section 2.4, such as the thermal stability and compatibility with Si process technology. Due to its potential of producing size controllable Si nanocrystals, the SRO/SiO₂ superlattice structure was chosen for this study. However, instead of using long annealing time at high temperature (~1100°C), the author implemented low-thermal budget annealing methods, such as rapid thermal annealing (RTA) and excimer laser annealing (ELA) processes. In addition, passivation method in the form of annealing in forming gas (FG) will also be discussed and compared to that of sample treated by prolonged annealing process. Such low thermal budget alternatives could offer more low cost alternatives to produce Si nanostructures in the SiO₂ matrix. Another supporting result on this approach is that the clustering of Si atoms has been established to take place during the first few minutes of annealing [4-21]. To the author's knowledge, the study of photoluminescence properties of rapid thermal annealed samples has not been well reported.

The Rapid thermal annealing (RTA) has not been used for fabrication of Si nanocrystals until recently. One of the recent examples is the implementation of RTA process prior to prolonged conventional annealing on bulk SRO structure to produce more uniform distribution of Si nanocrystal sizes and therefore reduce the full width half maximum (FWHM) of PL emission bands in a bulk Si-rich oxide (SRO) film [4-18]. Koukos et al. [4-18] reported that RTA process restricted the movement of Si atoms, thus favouring the formation of high density of small Si-nanoclusters. Their work however still relied heavily on the prolonged annealing at high temperature (~1100°C) and because the sample is bulk SRO, the PL peak wavelength cannot be easily controlled. On the other hand, the excimer laser annealing (ELA) method offers beneficial way to locally treat the sample without unintentionally heating the substrate. The effects of ELA method on the photoluminescence of Si nanocrystals have been reported by several authors [4-19], [4-120]. Daigil et al. [4-19] reported the work of ELA treatment on thermal annealed Si/SiO₂ superlattice samples and reported the enhancement of Si nanocrystals related PL peak intensity. Yeh et al. [4-20] reported the formation of Si nanostructures in amorphous Si (a-Si) by KrF excimer laser annealing and observed PL emission at 1.31 and 1.76 eV. However, the effect of excimer laser annealing on the formation of Si nanostructures in oxide material has not been well studied too.

Figure 4.1 The description of the cross-section view of SRO/SiO₂ superlattice structure

Figure 4.1 shows the cross-section of SRO/SiO₂ superlattice structure developed in this work. The terms “superlattice” refers to the periodical arrangement of SRO and SiO₂ layers. The periodic SRO and SiO₂ layers are clearly indicated. The top SiO₂ buffer was deposited to protect the superlattice structures from oxidation during thermal annealing in N₂ environment. To deposit the SRO/SiO₂ superlattice samples, the RF co-sputtering technique was used and it will be described in section 4.2.

The contents of this chapter are as follows. In section 4.2, the preparation scheme of SRO/SiO₂ superlattice samples, ranging from thin film deposition process to post-annealing process are described in detail. The characterization work of SRO/SiO₂ superlattice samples treated by low thermal budget processes is discussed in section 4.3. In this experimental work, Jipelec Rapid Thermal Processor (RTP) was used to perform RTA process on the SRO/SiO₂ superlattice samples. Using the SRO/SiO₂ superlattice structure, a better control of Si nanocrystals and thus emission peak is demonstrated and discussed in detail. To enhance the Si nanocrystals PL intensity, the hydrogen passivation was carried out and discussed. For comparison purpose, SRO/SiO₂ superlattice sample was also treated by long annealing process in a quartz tube. In section 4.4, another alternative annealing method, excimer laser annealing (ELA), using KrF excimer laser system operating at wavelength of 248 nm (5 eV) will be presented.

4.2 Preparation of Si-rich oxide/SiO₂ superlattice samples

In this section, the preparation of SRO/SiO₂ superlattice samples is described. The co-sputtering technique has been described in Chapter 2 section 2.3. The advantages and disadvantages

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of this technique over other deposition technique have also been highlighted in the same section. Prior to each deposition process, a 4" Si substrate was cleaned in ultrasonic bath. The ultrasonic treatment was applied to the Si substrate to remove any particles on the surface of Si substrate. The Si substrate was then rinsed by de-ionized water and dried with nitrogen (N₂) gun before loaded into sputter deposition chamber.

(a)

(b)

Figure 4.2 (a) Schematic of RF magnetron sputter deposition chamber. The angle of magnetron target with respect to normal line (n) is denoted as θ (b) Normalized thickness distribution of as-deposited SiO₂ sample on a 4" wafer. The tilting angle of magnetron target is 24° with respect to normal line (n).

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Figure 4.2(a) shows the schematic diagram of the sputter deposition chamber. The sputter deposition chamber consists of three magnetron sources located at the bottom of the chamber. The substrate holder is located on the top of the chamber connected to a heating element. The prepared Si substrate is held onto substrate holder facing downwards. Each magnetron target faces upward with an inclination angle $\theta=24^\circ$ with respect to vertical line. This inclination angle is the optimized angle to produce the good uniformity ($\pm 2\%$) over 2" diameter area, as shown in Figure 4.2(b). The diameter of each Si substrate prepared for deposition was 4" diameter.

Prior to the sputter deposition process, the chamber was pumped down to a base pressure of 10^{-7} Torr. The substrate was then heated at temperature of 250°C to outgas large percentage of deep water still existing in the chamber. This is important to suppress the concentration of hydroxyl group (O-H bonds) to achieve relatively dense as-deposited samples. The low concentration of OH is also important in view of Erbium (Er) doped SRO/SiO₂ superlattice samples, which is discussed in Chapter 6. It is established that O-H acts as absorption centre at $1.55\ \mu\text{m}$ which is usually attributed as one of the possible factors of Er emission quenching.

To deposit the SRO/SiO₂ superlattice and bulk SRO samples, two sputtering targets were used, namely Si and SiO₂ targets. SRO layer was deposited by sputtering Si and SiO₂ targets simultaneously and SiO₂ layer was deposited by sputtering SiO₂ target only. The sputtering gas was Ar with partial pressure of 6 mTorr. The top SiO₂ buffer layer was deposited to reduce diffusion of residual oxygen and thermal nitridation which might be present during the post-deposition annealing process. During the deposition process, substrate temperature was maintained at 100°C . To ensure uniformity, the substrate was rotated at 20 rpm. Prior to deposition process, each target was pre-sputtered at low power ($\sim 20\text{W}$) for 20 minutes to ensure the target is free of surface contamination.

Figure 4.3 The flow chart of deposition process of SRO/SiO₂ superlattice samples

The flow chart of deposition process of the SRO/SiO₂ superlattice samples is described in Figure 4.3. Firstly, the deposition rates of SiO₂ layers for different RF powers of SiO₂ target were determined. The atomic composition of the as-deposited SiO₂ layer was also determined. Secondly, the deposition rates of SRO layers for different RF powers of Si target were characterized while maintaining the RF power of SiO₂ target constant at 150 W. Furthermore, the Si concentrations in the deposited SRO layers were also characterized. Figure 4.4 shows the deposition rates of SiO₂ (left y-axis) and SRO layers (right y-axis) for different RF powers of SiO₂ (bottom x-axis) and Si (top x-axis) targets, respectively. The deposition rates of SiO₂ layer is ranging from 20 to 70 Å/minute when the RF power of SiO₂ target is varied from 60W to 200W. On the other hand, by varying the RF power of Si target from 60 W to 150 W (RF power of SiO₂ target constant at 150W) results in the increase of deposition rates of SRO layers, ranging from 65W to 150W. The deposition rate of the as-deposited sample was derived by simply dividing the thickness of as-deposited layer by the deposition time. The thickness of an as-deposited sample were obtained by measuring a thickness of a step profile (created by etching process) of the as-deposited samples using DEKTAK surface profiler. The surface profiler has been described in more detail in Chapter 3 section 3.2.2.3.

Figure 4.4 The deposition rate of SiO₂ layer (left y-axis) as a function of RF power of SiO₂ target (bottom x-axis). The deposition rate of SRO layer (right y-axis) as a function of RF power of Si target (top x-axis). During the deposition process of SRO layer, the RF power of SiO₂ target was maintained at 150W.

It is noted that the O₂ gas was not incorporated during the deposition of SiO₂ layer because the presence of oxygen plasma causes unavoidable oxidation on the surface layer of Si. This is commonly observed in the reactive sputtering process, i.e. sputtering process using reactive plasma in addition of Argon (Ar), such oxygen (O₂) and nitrogen (N₂). Since the objective here is to deposit superlattice structure, i.e. alternating layers of SRO and SiO₂, such oxidized surface poses a difficulty in ensuring constant excess Si concentration in SRO layer.

To assess the quality of SiO₂ layer here, two SiO₂ samples were deposited on high quality UV-grade fused Silica plate Corning 7980 glass substrates by sputtering of SiO₂ target only and combination of Si and SiO₂ targets. For comparison, several SRO samples were also deposited on the UV-grade fused Silica plate Corning 7980 glass substrate.

Sample ID	RF power of Si (Watts)	RF power of SiO ₂ (Watts)	As-deposited thickness (nm)	Si concentration (at. %)	Post-deposition annealing treatment
SL1	0	150 W	400	34	None
SL2	0	150W	400	33	O ₂ , 1000°C, 2 minutes
SL3	60 W	150W	380	46	None
SL4	80 W	150W	360	55	None

Table 4.1 The deposition parameters of samples SL1, SL2 SL3, and SL4. The concentrations of Si atoms in all samples are also presented.

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The detailed descriptions of the samples were listed in Table 4.1. The composition of RF powers of Si and SiO₂ during the sputter deposition and Si concentration is presented. The Si concentrations of the samples were obtained by X-ray photoelectron spectroscopy (XPS) technique, which has been described in Chapter 3 section 3.2.2.2. After deposition process, all samples were not annealed except sample SL2 which was annealed in oxygen (O₂) environment at 1000°C for 30 minutes.

Figure 4.5 UV-Visible transmission spectra of samples SL1, SL2, SL3, and SL4

Figure 4.5 shows the UV-VIS transmission spectra, ranging from 190 to 900 nm, of samples SL1, SL2, SL3, and SL4. As the Si concentration of the sample increase from 46 at.% (s1) to 55 at.% (s4), the UV transmission edge is red-shifted, which means that the optical band gap decreases with increasing Si atomic concentration in the samples. The UV transmission edge of the oxidized sample (SL2) is blue-shifted as compared to that of sample SL1. It is observed that there is no large difference of UV-transmission edge for these two samples (SL1 and SL2). Furthermore the measured refractive indices of the as-deposited and oxidized SiO₂ films were ~1.47 and ~1.46 at 632 nm respectively. The similar refractive indices of the two samples show that the as-deposited sample SL1 are relatively close to stoichiometric SiO₂ films. The measurement of refractive indices of the samples was carried out using spectroscopic ellipsometry (SE) technique, which has been described in Chapter 3 section 3.2.1.3.

Lastly, when the deposition rates of SRO, and SiO₂ layers used have been characterized, the SRO/SiO₂ superlattice samples were deposited. Throughout all superlattice samples, the SiO₂ layers in the superlattice structure were maintained at 5 nm. On the other hand, the Si concentrations and thicknesses of SRO layers were varied to optimize the photoluminescence (PL) intensity. The samples were subjected to the low thermal budget process such as rapid thermal annealing (RTA) and excimer

laser annealing (ELA) process. The PL spectra of the SRO/SiO₂ superlattice samples by RTA and ELA processes will be discussed in the sections 4.3 and 4.4 respectively.

4.3 The effect of rapid thermal annealing of SRO/SiO₂ superlattice samples

The as-deposited SRO/SiO₂ superlattice samples were heated using the RTA and conventional annealing process. Subsequently, the Photoluminescence (PL) characterization was performed for all samples. In order to promote the growth of Si nanocrystals, the rapid thermal annealing (RTA) process was carried out on the SRO/SiO₂ superlattice samples. The profile of the RTA steps process which was used to treat the samples is shown in Figure 4.6.

Figure 4.6 Rapid thermal annealing (RTA) step profile for post-annealing treatment process

For comparison, a cut from each as-deposited superlattice sample was annealed in tube furnace under flowing N₂ gas at 1100°C for 2 hours. The Photoluminescence (PL) spectra of the annealed SRO/SiO₂ superlattice samples were measured at room temperature using Fluorog-3 Photospectrometer with broadband Xenon lamp as excitation source. The description of Fluorolog-3 Photospectrometer has been presented in Chapter 3 section 3.2.1.4.1. PL lifetime of the samples were measured by SPEX 1934D Phosphorimeter (Si-nanocrystals related emission decay) and Edinburgh instruments FL92 (defect related emission decay), which has been described in Chapter 3 section 3.2.1.4.4. JEOL 2100F Transmission Electron Microscopy (TEM), described in Chapter 3 section 3.2.2.1, was used to characterize the nanocrystals size.

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Sample ID	RF power of target (W)		Si concentration in SRO layer (at. %)	SRO layer thickness (nm)	No. of periods	Total as-deposited thickness (nm)
	Si	SiO ₂				
A1	60	150	38	3	50	530
A2	80	150	46	3	50	530
A3	120	150	55	3	50	530

Table 4.2 Deposition parameters of SRO/SiO₂ superlattice samples A1, A2, and A3, which have different Si concentration in SRO layers.

Three SRO/SiO₂ superlattice samples with different concentrations (at.%) of Si in SRO layers were deposited on Si substrates. The thicknesses of SRO layers of the three superlattice samples (A1, A2, and A3) are constant. The deposition parameters are listed in Table 4.2.

Figure 4.7 PL peak wavelengths (left y-axis) and intensities (right y-axis) of SRO/SiO₂ superlattice samples (A1, A2, and A3) for different Si concentration (at.%) in SRO layers. All samples were treated by RTA in N₂ environment at 1000°C for 2 minutes.

Figure 4.7 shows the PL peak wavelength (left y-axis) and PL peak intensity (right y-axis) of SRO/SiO₂ superlattice samples for different Si concentrations (at.%) in SRO layers after RTA process in N₂ at 1000°C for 2 minutes. The atomic composition of Si and O in SRO layer was characterized by the x-ray photoelectron spectroscopy (XPS). The thicknesses of SRO and SiO₂ layers in all three samples are constant at 3 nm and 5 nm, respectively. The PL peak wavelength is red-shifted as the Si

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concentration increases. This is because the increase of Si concentration means that more excess Si atoms that can cluster together to form larger nanocrystals through a thermal induced phase separation process of Si clusters and SiO₂ matrix, which can be described by this formula:

$$\text{SiO}_x \rightarrow \frac{x}{2}\text{SiO}_2 + \left(1 - \frac{x}{2}\right)\text{Si} \quad (4.1)$$

The increase of the size of Si nanostructures causes the PL peak red-shift. This effect is well known as quantum confinement (QC) effect, which has been explained in Chapter 2 section 2.2.2.2. On the other hand, the increasing trend of PL intensity as a function of Si concentration can be related to two factors, which are (i) the increase of absorption cross section of Si nanostructures with increasing size [4-6], and (ii) density of optically active Si nanostructures.

It is observed that the optimum PL intensity after rapid annealing for 2 minutes occurs for the sample with Si concentration of 46 at.% (RF powers of Si and SiO₂ targets of 80W and 150W, respectively) in the SRO layers. This deposition condition was used for deposition of SRO/SiO₂ superlattice samples with different thicknesses of SRO layers to study the effect of low budget thermal processes (RTA and ELA processes) on the controllability of PL peak wavelength of the superlattice samples with different thickness of SRO layers.

4.3.1 Si-nanocrystals related photoluminescence

To study the Photoluminescence (PL) of Si-nanocrystals (Si-nc) developed in this project, the thickness of the SRO layers were varied from 3 nm to 5 nm to control the Si nanocrystal sizes while the thickness of SiO₂ layers were kept constant at ~5 nm for all samples. The SiO₂ layer was maintained at 5 nm thickness to avoid the effect of SRO/SiO₂ interface roughness which could destroy the “self-arrangement” effect of Si-nanocrystals during annealing, as reported by Zacharias et al. [4-14].

Sample ID	SRO thickness (nm)	No. of periods	Total as-deposited thickness (nm)	Average nanocrystal size (N ₂ , 1000°C, 2 minutes); accuracy of ±0.5 nm
1	3	50	530	3.6
2	4	42	500	4.6
3	5	34	510	6

Table 4.3 Physical properties of SRO/SiO₂ superlattice samples

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Table 4.3 presents the SRO and SiO₂ layer thickness, number of periods of SRO/SiO₂ layers, total thickness of the as-deposited samples and the average size of nanocrystals after annealing at 1000°C in N₂ ambient of samples 1, 2 and 3. All samples were deposited to similar thickness of ~500 nm. As expected, from the cross-section transmission electron microscopy (TEM) characterization of sample 1, 2, and 3, the average size of Si nanocrystals increases with the increase of the thickness of SRO layer. The TEM of sample 1 is shown in Figure 4.8. The Si nanocrystals with average size of 3.6 nm can be seen clearly from the lattice fringes (enclosed by the circles). The Si-nanocrystals are formed in the original SRO layer due to RTA process. In addition, the SiO₂ layers separating two SRO layers are also indicated.

Figure 4.8 TEM image of sample 1 after RTA process in N₂ environment at 1000°C for 2 minutes. The average size of Si nanocrystals is 3.6 nm.

Figure 4.9 PL spectra (350-900 nm) of SRO/SiO₂ superlattice samples (samples 1 to 3) treated by RTA at 1000°C in N₂. The PL spectra in general consists of three bands, PL 'a', PL 'b', and PL 'c'.

Figure 4.9 shows the PL spectra of samples 1, 2 and 3 after RTA process at 1000°C for 2 minutes in N₂ atmosphere. In general, three dominant PL emission band were observed. PL emission bands around 400 nm, 515 nm and 768 nm are denoted by PL 'a', PL 'b', and PL 'c', respectively. PL 'c' is red-shifted as the thickness of as-deposited SRO layer is increased (see Table 4.3).

As shown in Figure 4.9 and Table 4.3, the PL 'c' peak wavelengths of samples 1, 2 and 3 are 768 nm (1.61 eV), 798 nm (1.55 eV), and 812 nm (1.52 eV) for Si nanocrystal sizes of ~3.6 nm, 4.5 nm, and 6 nm, respectively. Such trend has been reported for conventional furnace annealing of bulk SRO film [3-7]. This result is consistent with previous studies that nanocluster is effectively formed in the first few minutes of annealing process [4-18], [4-21], [4-23]. Such a small variation in PL peak energy agrees well with semi-empirical work by Wolkin et al. [4-22] which demonstrated that nanocrystals with diameters larger than 3 nm have PL peak energies following closely the quantum confinement effect. This is further supported by the absence of consistent PL peak around 1.6 eV (775 nm) commonly responsible for oxygen-defect related "red PL" [4-24]-[4-26]. Wolkin et al. investigated the role of oxygen passivation in porous Si nanostructure and demonstrated that the effect of oxygen passivation on the nanocrystals surface was increasingly dominant as the nanocrystals size decreases. On the other hand, according to Wolkin, theoretically and experimentally, for relatively

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large nanocrystal (diameter > 3nm), such as that of the samples in this work, the Si=O bonds, which dominantly present on Si-nc/SiO₂ interface, does not affect the quantum confinement related PL peak energy (PL 'c' in Figure 1) [4-22]. At present, a fair comparison with other literature is difficult due to lack of similarity of the structure in other works. Khriachtchev et al. [4-23] reported the annealing induced PL of Si/SiO₂ superlattices on Si substrate at 600 nm after RTA at 1200°C for 5 s. The observed PL peak position is different from that in this work. Khriachtchev et al. attributed the PL peak to Si=O covalent bonds in the Si/SiO₂ network.

It is also observed that PL 'c' of sample 3 (thickest SRO layer and hence the largest Si nanocrystal size) in Figure 4.9 has the weakest intensity among samples 1 to 3. This is because the annealing time required to form nanocrystals is higher for thicker SRO layer, which results in lower concentration of good quality nanocrystals in the samples formed by the annealing process.

Figure 4.10 TEM image of sample 1 after annealing at (a) 700°C resulting in amorphous nanoclusters and (b) 1000°C, characterized by nanocrystalline lattice (top-left corner inset)

Figure 4.10(a) and 4.10(b) show the formation of Si nanoclusters upon annealing at 700°C and 1000°C, respectively. It shows that nanocrystal has been formed even when samples are annealed for only 2 minutes. Furthermore, by comparing Figure 4.10(a) and 4.10(b), it is obvious that nanostructure size of sample 1 increases from 2.8 nm to 3.64 nm with increasing RTA temperature from 700°C to 1000°C.

4.3.2 The defect states related photoluminescence

In this section, the author will further discuss the Photoluminescence (PL) bands, PL 'a' and 'b' mentioned above, which are related to defect states.

(a)

(b)

Figure 4.11 PL spectra (a) and PLE spectra (b) of sample 1 as annealed at temperature of 500°C-1000°C, in N₂ environment. In (a), for each PL band (PL 'a', PL 'b', and PL 'c'), dotted lines tracing PL peaks serves as a guide-to-eye. Each PLE spectrum (b) is monitored at wavelength λ_m , as indicated.

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Figure 4.11(a) represents PL spectra of sample 1 as a function of RTA temperature, from 500°C-1000°C. It appears that PL 'c' peak position after annealing at 900°C is at longer wavelength than PL 'c' after annealing at 1000°C. This appears to be inconsistent with general TEM characterization results, which shows that the clusters size grows with increasing annealing temperature. However, such similar observation of PL spectra is also reported by L X Yi et al. [4-27] based on their work on long annealing treatment of SiO/SiO₂ superlattice deposited by the evaporation technique. They attributed this observation to amorphous Si nanostructures. For a similar size, amorphous nanostructures have smaller effective band gap than its crystalline nanostructures due to its disordered structure [4-27].

After discussing the behaviour of PL 'c', the author will now discusses PL 'a' and PL 'b'. In Figure 4.9, the author observes that PL 'a' and PL 'b' do not have size-dependent effect, marked by the non-existence of the PL peak-shift across the samples with different nanocrystal sizes. They are possibly related to defects due to oxygen deficiency [4-28], [4-29] or some other defects on the surface of nanocrystals or in the oxide matrix. However, the PL 'a' and 'b' peak positions do change (blue-shifted) as a function of annealing temperature, as shown in Figure 4.11(a). PL 'b' in particular shows strong shift upon annealing temperature from 700°C-1000°C. Its intensity also increases with increasing annealing temperature, from 500°C to 1000°C. In order to understand the origin of this PL, the lifetime of PL 'a' and 'b' were measured to be around ~2 ns. Such a short lifetime is in agreement with other work reported by Tsybeskov et al. [4-30], indicating that the two PL bands are indeed defect related, and not due to exciton recombination. The PL 'b' is possibly originated from the deficiency of oxygen species usually attributed to E' defect, which presents as an unpaired spin delocalized over five Si atoms [4-28], [4-31], [4-32]. PL 'a' could also be related to oxygen related defect in the form of weak oxygen bonding, indicated by reduction of intensity as annealing temperature increases [4-28]. Indeed, PL 'a' and PL 'b' intensity were reduced when annealed in oxygen environment. The details of this work are discussed in Chapter 5. On the contrary, Svrcek et al. [4-33] reported in their work that blue PL (427 nm) was originated from quantum confinement effect and surface defects. However, their preparation method is different with ours. Furthermore, the average size of nanocrystals in their work is relatively smaller (~2 nm) where surface effect might become more dominant, as pointed out by Wolkin et al. [4-22].

Photoluminescence Excitation (PLE) spectra at various RTA temperatures monitored at peak positions of PL 'b' and PL 'c' in Figure 4.11(a) is shown in Figure 4.11(b). Three different absorption bands are observed and denoted as PLE 'a' (342-302 nm, or 3.61 - 4.1 eV), PLE 'b' (380-364 nm, or 3.26 - 3.4 eV) and PLE 'c', which consists of a series of multiple absorption peaks at 395 nm (3.14 eV), 422 nm (2.94 eV), 439 nm (2.82 eV), 451 nm (2.75 eV), and 467 nm (2.65 eV). Note that the peak of the PLE 'b' band of the PLE spectrum monitored at PL 'c' cannot be shown because of the

second harmonic effect. This truncation of PL spectrum data has been explained in Chapter 3 section 3.2.1.4.1. Nevertheless, the indication of the presence of a band is obvious in Fig 4.11(b). PLE 'a' and 'b' only appear significantly after RTA at 700°C when numerous amorphous nanostructures with average size of 2.8 nm were observed (see Figure 4.10(a)). It can also be observed that PLE 'a' and 'b' are close to two of direct optical transitions widely established in bulk Si crystal, $\Gamma_{25'}-\Gamma_{15}$ (3.4 eV), $\Gamma_{25'}-\Gamma_2$ (4.2 eV) [4-34], [4-35]. The presence of PLE 'a' and PLE 'b', when the samples were monitored at PL 'c', indicates that the transitions involve Si nanocrystals. The PLE 'a' and 'b', which appears when the samples were monitored at PL 'b' indicates that the transitions involve oxygen related defects. Therefore, it is likely that the PLE 'a' and 'b' transitions are due to the oxygen related defects at the surface or close to the Si nanocrystals. Furthermore, upon oxygen annealing, when monitored at PL 'c', PLE 'a' and PLE 'b' intensity is higher compared to those of the samples without oxygen annealing. The effect of the oxygen annealing on the PL spectra will be discussed in more detail in Chapter 5.

4.3.3 Constructing the energy diagram of Si nanocrystals

Based on PL and PLE spectra in Figure 4.11(a) and 4.11(b), respectively, the energy diagram was constructed and shown in Figure 4.12. The Si nanocrystals related radiative transition is obtained from PL 'c' emission in Figure 4.11(a). From Figure 4.11(b), when the samples were monitored at PL 'c' (768 nm), PLE 'a' and PLE 'b' bands were observed. In Figure 4.12, these excitations are presented as upward transitions to bands a and b described in the Si nanocrystals energy diagram. The position of the Si nanocrystals energy levels in the band gap of the SiO₂ is taken from literature [4-35]. Prior to the radiative recombination at PL 'c', the electrons relax non-radiatively to the lowest LUMO (lowest unoccupied molecular orbital) and then relax radiatively to HOMO (highest occupied molecular orbital). When the samples were monitored at PL 'b' (at 515 nm), the PLE 'a', PLE 'b' and PLE 'c' were observed (see Figure 4.11(b)). As discussed above, these transitions are associated with the oxygen related defects. In Figure 4.12, they are presented as upwards transitions in oxygen related defects energy diagram. The excited electrons relax nonradiatively and then radiatively recombine at 2.65 eV and 2.4 eV for PL 'a' and PL 'b' respectively.

Figure 4.12 Energy diagram of SRO/SiO₂ superlattice (sample 1) annealed by RTA at 1000°C for 2 minutes. Three types of transitions are the non-radiative de-excitation (curved arrowed line), excitation (upward) and radiative emission (downward) transition. Bands a', b', c' (related to absorption) and bands a, b, c (related to emission). The construction of the energy diagram is started with Si nanocrystal related transitions.

Investigation of PL and PLE spectra of rapid thermal annealed SRO/SiO₂ superlattice structure helps understand the main absorption and emission energy levels involved in room-temperature PL. Numerous Si nanoparticles with average diameters of ~3.64-6 nm were observed by TEM after RTA at 1000°C in N₂ ambient, demonstrating possibility of low thermal budget alternative for nanocrystal formation. Transition from amorphous to crystalline nanostructures occurs when RTA temperature is increased to 1000°C.

4.3.4 The effect of Hydrogen passivation

In order to enhance the PL intensity of the samples which have been treated by RTA process in N₂, at 1000°C for 2 minutes, the author further studied the effect of passivation by annealing the RTA-treated samples in the forming gas (FG) with gas composition of 5%H₂ and 95% N₂ at temperatures of 500°C.

Figure 4.13 The PL intensity of sample 1, 2, and 3 after RTA (in N₂ at 1000°C for 2 minutes) only, RTA with H-passivation (RTA, N₂, 1000°C, 2 minutes followed by 5%H₂:N₂, 500°C, 30 minutes), and long annealing (N₂, 1100°C, 2 hours)

The forming gas or FG (5%H₂:N₂) annealing at 500°C for 30 minutes was used to passivate the Si nanostructures. At such annealing temperature in FG, hydrogen is an effective way to passivate any dangling bonds or defect present in the sample. Therefore, the annealing process in FG will be referred to as H-passivation. This H-passivation was carried out in the tube furnace at 1 sccm flow rate of FG. Prior to the passivation treatment, the tube furnace was purged using FG for 30 minutes. The PL intensity of samples after H-passivation increases by a factor of ~8 as compared to that of RTA-treated samples.

Figure 4.13 shows the Si-nanocrystals related PL peak intensity of superlattice samples treated by RTA process (in N₂ ambient at 1000°C for 2 minutes) with and without passivation treatment, which are indicated as RTA+HP and RTA respectively. In addition, the PL peak intensity of the samples annealed in tube furnace in N₂ ambient, at 1100°C for 2 hour, which is indicated as CA, is also presented for comparison. The PL peak wavelengths were not shifted upon H-passivation. Furthermore, it is observed that the PL peak intensity of the samples treated by RTA and H-passivation is higher than that of samples annealed in long period using conventional tube furnace (CA) by a factor of ~1.5-1.7. Such a consistent increase of PL intensity after H-passivation can be related to the passivation of Pb-defect, i.e. Si dangling bonds which are usually formed in Si/SiO₂ interface. This type of defect centre has been widely reported to be responsible for “optically dark” Si-nc [4-36] due to its high non-radiative recombination rate. The fact that the PL intensity of the samples after H-passivation is higher than that of the samples treated by long conventional annealing

(N₂, 1100°C, 2 hours) means that there are still a percentage of “optically” dark Si nanocrystals even after long annealing treatment.

The combination of RTA and H-passivation on SRO/SiO₂ superlattice samples has been demonstrated to be a viable alternative method to produce light emitting Si nanocrystals with good controllability.

4.4 The Effect of excimer laser annealing on photoluminescence

After studying the effect of rapid thermal annealing (RTA) and hydrogen passivation processes of the SRO/SiO₂ superlattice samples on the Si-nanocrystals related PL spectra, the author further investigated the effects of excimer laser annealing (ELA) of the SRO/SiO₂ superlattice samples. The major advantage of ELA is heat localization which is extremely useful for the case of substrate materials with low thermal stability [4-37], [4-38]. In order to do this, the SRO/SiO₂ superlattice samples were exposed to KrF excimer laser at 248 nm which has an effective cross section dimension of 2.5 cm x 1.4 cm. The pulse duration was about 25 ns and the frequency was 10 Hz.

In this study, the ELA treatment was carried out on the as-deposited samples and annealed samples (RTA process in N₂ at 1000°C for 2 minutes) prior to ELA treatment. After ELA treatment, both types of samples were annealed at 120°C in vacuum for 30 minutes to anneal out defects. The photoluminescence (PL) of the samples were measured using Fluorolog-3 spectrometer with excitation line selected at 325 nm.

4.4.1 Excimer laser annealing for the as-deposited SRO/SiO₂ superlattice samples

Figure 4.14(a) shows the PL spectra of sample 1 (3 nm SRO layer) after ELA treatment using 40 mJ/cm² for different pulse counts. In this figure, the small PL shoulder observed at 366 nm is attributed to emission from Si substrate. It is also observed that prior to excimer laser annealing (ELA) treatment the as-deposited SRO/SiO₂ superlattice samples have a very weak PL band at 400-550 nm. As the laser pulse counts increases, the PL intensity monotonously increases without any significant changes in the PL spectral shape and peak wavelength. The lifetime of the PL at 450 nm was measured using Edinburgh Instrument FL92 system to be around ~2 ns. This suggests that the PL band at 450 nm is related to defect states. From Figure 4.14 (a), it is observed that sample 1 which was exposed by 10000 KrF laser pulse counts exhibit PL intensity relatively much stronger than that

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of as-deposited samples without any PL peak shift, indicating that the increase of pulse counts (the increase of exposure time) results in the increase of density of optically active defect centres.

Figure 4.14 (a) PL spectra of SRO/SiO₂ superlattice samples upon ELA treatment using 150 mJ for different pulse counts. (b) PL spectra of SRO/SiO₂ superlattice samples upon ELA process using power of 40mJ/cm² for pulse counts of 1000.

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The PL spectra of SRO/SiO₂ superlattice samples with four different SRO thicknesses: 3 nm, 4 nm, 4.5 nm, 5.5 nm was presented in Figure 4.14(b). In these samples, the thickness of SiO₂ layer is 5 nm.

In general, three important PL bands centred at ~400 nm, ~450nm and ~530 nm were observed. These emission bands are defects related PL. There is however no Si-nanocrystals related PL band observed for all samples. The absence of Si-nanocrystals is probably because the as-deposited samples were exposed to 248 nm KrF laser but in a very short duration. Although the equivalent temperature due to excimer laser exposure might be high, the exposure time for 1000 pulses of ELA is equivalent to $10000 \times 25 \text{ ns} = 0.025 \text{ ms}$, relatively much shorter time than 2 minutes of rapid annealing employed in this work. The short total exposure time of KrF laser provides insufficient diffusion time for formation of Si nanostructures.

Exposure of sample to laser fluence larger than 130 mJ/cm^2 damages the surface of as-deposited sample. The damaged pattern follows the beam profile closely, i.e. the sample surface was damaged right at the centre where the laser beam intensity is at maximum. It is noted that the damage was observed only for as-deposited sample. The author believes that localized heating at nanoseconds range induced large thermal stress especially at the surface.

4.4.2 Excimer laser annealing for the as-annealed SRO/SiO₂ superlattice samples

In this experiment, SRO/SiO₂ superlattice samples were annealed in N₂ at 1000°C for 2 minutes prior to exposure by 248 nm KrF laser. “As-annealed” sample refers to sample that was annealed using RTA in N₂ at 1000°C for 2 minutes.

Figure 4.15 Sample N18 annealed at N₂, 1000°C, 2 minutes and exposed to KrF laser for different laser fluences: 40 mJ/cm², 90mJ/cm², and 130mJ/cm². The excimer laser pulse counts were kept constant at 1000 for each ELA treatment.

As discussed in section 4.4.1, upon excitation at 325 nm, the as-annealed samples exhibit three PL bands at 450 nm (PL 'a'), 530nm (PL 'b'), and ~800 nm (PL 'c'). The first two bands are related to oxygen deficiency defects, whereas the third band is related to Si nanocrystals. Figure 4.15 shows the PL spectra of SRO/SiO₂ superlattice samples as a function of laser fluence with the number of pulse fixed at 1000 counts. PL intensities at 450 nm (PL 'a') and 530 nm (PL 'b') are reduced to a negligible intensity after ELA fluence of 130mJ/cm². In general, a consistent reduction of all PL bands as a function of laser fluence was observed. In particular, Si nanostructures related PL intensity at ~800 nm was also consistently reduced as a function of fluence ranging from 40mJ/cm² to 130mJ/cm². The reduction of defect and Si-nc related PL intensities indicates the formation of non-radiative defect states.

4.5 Summary

In this chapter, the author has discussed the development of Si-rich oxide (SRO)/SiO₂ superlattice structure, which consists of (i) deposition process of the superlattice samples, (ii) the study of the effect of rapid thermal annealing (RTA) with and without hydrogen passivation on the PL spectra related to Si nanocrystals and also defect states. (iii) the study of the effect of excimer laser annealing (ELA) on the Photoluminescence (PL) spectra. In section 4.3, it was demonstrated that RTA process of SRO/SiO₂ superlattice samples in N₂ environment at 1000°C for 2 minutes produced

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Si-nanocrystals related PL bands with peak varied 768 nm to 812 nm for different Si nanocrystals sizes, ranging from 3.6 nm to 4.6 nm. The PL peak wavelength and the size of nanocrystals were successfully controlled by the thickness of SRO layer. In addition, two oxygen deficiency defect-related PL bands at 400 nm and 515 nm were also observed. The Si nanocrystals related PL intensity at ~800 nm can be further enhanced by hydrogen passivation by annealing in forming gas (5%H₂:N₂) at 500°C for 30 minutes. With passivation, the PL intensity of the samples was enhanced by a factor of 8 as compared to that of the rapid annealed samples. Furthermore, the PL intensity of the passivated samples was higher by a factor of 1.5 to 1.7 as compared to that of the samples treated at long annealing process. Hydrogen passivation reduces competing non-radiative recombination centers, most notably Pb-defects which are formed on the interface of Si nanostructures/nanocrystals and matrix. With hydrogen passivation, there was no PL peak-shift observed. In section 4.4, the PL characterization of KrF excimer laser annealing is presented. It is demonstrated that KrF excimer laser cannot be used to effectively form Si nanostructures due to short exposure time. On the contrary, excimer laser annealing reduces the PL intensity of Si-nc related emission. Based on these results, the formation of Si nanostructures after annealing of SRO/SiO₂ superlattice samples can be used for further carried out several works, such as the effect of oxygen annealing on Si-nc average size.

Chapter 5

Size Control of Silicon Nanocrystal by Two-step Rapid Annealing Treatment

5.1 Introduction

In the previous chapter, the author has presented and discussed the photoluminescence (PL) spectra of the SRO/SiO₂ superlattice structure by low-thermal budget methods, namely rapid thermal annealing (RTA) and excimer laser annealing (ELA) processes. In the case of ELA-treated samples, there were only defect-related PL bands observed. On the other hand, upon rapid thermal annealing (RTA) treatment, the samples exhibited PL bands related to Si-nanocrystals and defect states. A consistent red-shift of Si-nanocrystal related PL peak energy corresponding to the increasing average size of nanocrystals was observed and attributed to quantum confinement effect (QCE). On the other hand, the defect-related PL peak energies are fixed across different average size. Furthermore, the enhancement of Si-nanocrystals related PL intensity attributed to hydrogen passivation has also been discussed.

A post-deposition method for controlling the PL peak wavelength was investigated and developed in this work. Based on the established quantum confinement effect, PL peak wavelength can be tailored by controlling the size of the existing Si-nanocrystals. In this chapter, the author focuses on the implementation of rapid oxidation method to control the average size of Si nanocrystals. In the oxidation process, oxygen diffuses from the top surface into the bulk of the sample, leading to size reduction of the existing Si-nanocrystals. Several works on the oxidation method of Si-nanocrystals have been reported elsewhere and discussed as follows. Firstly, a method proposed by Photopoulos et al. [5-1], is the successive deposition and oxidation of nanometric amorphous Si/SiO₂ layer to form Si-nanocrystal/SiO₂ superlattice structure. This method, however, requires a long oxidation time for each layer and therefore it takes much longer total annealing time to achieve relatively thick Si-nanocrystal/SiO₂ superlattice structure. Furthermore, there was lack of lateral confinement of the Si-nanocrystals formed by this method. Secondly, another method reported by Brongersma et al. [5-2] is by oxidizing the Si-nanocrystals embedded in SiO₂ matrix. In their work, Si-nanocrystals formed in a thermally grown SiO₂ were introduced by Si implantation followed by annealing at 1100°C for 1 hour. The size reduction of Si-nanocrystals was realized by oxidation process at temperature of 1000°C and PL peak wavelength can be blue-shifted to about ~680 nm after

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oxidation for 29 minutes. At such oxidation temperature and time, PL intensity was reduced greatly as the concentration of Si-nanocrystals was reduced significantly, as indicated by the reduction of Si profile from Rutherford Backscattering Spectroscopy (RBS) characterization results of their samples.

From the results of RTA treatment of superlattice samples previously discussed in Chapter 4, the author investigated the two-step RTA process of SRO/SiO₂ superlattice samples. The details of the RTA process and the resulting photoluminescence (PL) spectra will be discussed in section 5.2 and 5.3, respectively. In section 5.4, further enhancement of Si-nanocrystals related PL intensity using long annealing in air at temperature lower than oxidation temperature will be discussed. Using this method, the average size of silicon (Si) nanocrystals can be controlled without the need to tailor the thickness of SRO layers during deposition process.

5.2 Two-step rapid annealing of SRO/SiO₂ superlattice structures

In this work, three SRO/SiO₂ superlattice samples were deposited by rf magnetron co-sputter deposition method. The physical properties of the three superlattice samples are described in Table 5.1. The atomic composition O to Si in SRO layer is determined by X-ray Photoelectron Spectroscopy (XPS) to be 1.2. The three samples were denoted by samples A, B, and C. The thicknesses of SRO layers of samples A, B, and C are 3, 4, and 5 nm, respectively, while the numbers of periods of alternating layers (SRO/SiO₂) of samples A, B, and C are 50, 42, and 38, respectively. The number of period of alternating layers was chosen to maintain similar thickness across all samples of about ~500 nm. The deposition process parameters for the SRO/SiO₂ superlattice structure have been described in Chapter 4 section 4.2.

Sample ID	SRO thickness (nm)	Number of periods	Total as-deposited thickness (nm)	Average nanocrystal size (N ₂ , 1000°C, 2 minutes); accuracy of ±0.5 nm
A	3	50	530	4
B	4	42	500	4.6
C	5	34	510	6

Table 5.1 Physical properties of SRO/SiO₂ superlattice samples

The author employed a low-thermal budget process to control the size of Si nanocrystals in the form of two-step rapid annealing process consisting of: i) process ‘1’ which is RTA process at 1000°C in N₂ environment for 2 minutes, and ii) process ‘2’ which is RTA process at 600°C, 700°C, 800°C, and 900°C in O₂ environment for 1-10 minutes. The samples annealed using the process ‘1’

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only are referred to as “as-crystallized” sample, whereas the samples annealed using both processes ‘1’ and ‘2’ are referred to as “oxidized” samples.

Figure 5.1 RTA process profile for oxidation process of Si-nanocrystals/SiO₂

The RTA process steps profile for process ‘1’ was described earlier in Figure 4.6 in the Chapter 4, whereas that for process ‘2’ was described in Figure 5.1. All rapid annealing and oxidation treatments were performed using JIPELEC Rapid Thermal Processor (RTP). The rapid oxidation process (process 2) was carried out immediately after process 1. Prior to oxidation process, the RTP chamber were purged with oxygen (O₂) flow for several cycles at room temperature.

5.3 Photoluminescence characterization of oxidized samples

The photoluminescence (PL) characterization is one of the most direct methods to investigate the optical properties of Si-nanocrystals. In the following section, the PL analysis was used to relate the oxidation parameters (temperature and time) to the average size of Si nanocrystals. The PL spectra of all samples were measured using Fluorolog-3 system, with excitation line fixed at 325 nm. A more detailed description of Fluorolog-3 system has been described in Chapter 3 section 3.2.1.4.1. The PL lifetime measurement was carried out using Edinburgh Instrument FL92 (nanoseconds range) and SPEX 1934D Phosphorimeter (microseconds range). Both systems have been described in Chapter 3 section 3.2.1.4.4. JEOL 2100F Transmission Electron Microscopy (TEM), which has been described in Chapter 3 section 3.2.2.1, was used to characterize the Si nanocrystals size in the samples

5.3.1 Photoluminescence dependence on oxidation temperature

The samples were oxidized at temperatures lower than the onset temperature for crystallization (1000°C). The range of oxidation temperature from 600°C to 900°C was selected. The dependence of PL spectra on oxidation temperature is discussed as follows.

Figure 5.2 PL spectra of sample A after annealing at N_2 , 1000°C, 2 minutes (1) and subsequent oxidation for 2 minutes at different temperatures: (2) 600°C, (3) 700°C, (4) 800°C, (5) 900°C

Figure 5.2 shows the PL behaviour of sample A which is oxidized for 2 minutes at temperatures from 600°C to 900°C. For comparison, the PL of as-crystallized sample is also included. The as-crystallized sample has three different main PL emission bands: 400 nm, 515 nm, and 780 nm. It is noted that in all measured PL spectra, the spectrum containing second harmonic of the excitation wavelength, ranging from 630 to 670 nm, could not be taken. This has been explained in Chapter 3 section 3.2.1.4.1. The first two PL bands at 400 nm and 515 nm are attributed to defect states in the oxide matrix or near the Si nanocrystal/ SiO_2 interface. The evolution of these two PL bands upon RTA process in N_2 environment has been discussed in chapter 4 and has been reported in publication [5-3]. In general, they are attributed to oxygen deficiency in silica matrix, as confirmed by the very short emission lifetime (~ 2 ns range). On the other hand, PL at 780 nm is attributed to Si-nanocrystals, and from now onwards referred to as nc-PL band.

It is observed in Figure 5.2 that the PL at 780 nm peak position is blue-shifted and the intensity increases, with increasing oxidation temperature from 600°C to 800°C. This consistent nc-PL peak blue-shift is attributed to the reduction of Si nanocrystal size, as confirmed by the transmission electron microscopy (TEM) technique. For example, oxidation process at 800°C for 2 minutes reduces the nanocrystals size of sample A from ~ 4 nm (as-crystallized) to ~ 3.2 nm, as shown in Figure 5.3(b) and 5.3(c).

Figure 5.3 (a) Illustration of oxidation mechanism of Si-nanocrystals [5-4], TEM image of (b) as-crystallized and (c) oxidized (at 800°C for 2 minutes) sample A

Figure 5.3(a) shows the size reduction mechanism of Si-nanocrystals which was well demonstrated by Sheer et al. [5-4] using characterization techniques such as Energy Filtered Transmission Electron Microscopy (EFTEM) and X-ray Photoelectron Spectroscopy (XPS) techniques. In the as-crystallized sample, the Si nanocrystals are usually separated from the surrounding stoichiometric oxide (SiO_2) by Si suboxide, SiO_x ($x < 2$) shells. Upon oxidation, the size reduction of Si-nanocrystals was accompanied by the oxidation of SiO_x shell into a stoichiometric SiO_2 shell encapsulating the Si-nanocrystals. The nanocrystal size reduction as a function of oxidation

temperature from 600°C to 800°C can be explained using the model proposed by Kao et al [5-5]. In the proposed model, the compressive stress, which occurs due to volume mismatch of Si and SiO₂, is directed normal to the Si/SiO₂ interface and prevent further oxidation of the Si-nanocrystals. Therefore using this model [5-5], it can be explained that the surrounding oxide matrix is more viscous at oxidation temperature of 800°C than that at 700°C and 600°C, leading to further oxidation and reduction of Si nanocrystal size.

Furthermore, the increment of PL intensity as a function of oxidation temperature, ranging from 600°C to 800°C, can be explained as follows. It is known that Si-nanocrystals emitting at different wavelengths have different absorption and emission cross sections. At a fixed wavelength, the changes in nc-PL intensity can be related to: (i) the changes in the density of Si-nanocrystals of particular size and/or (ii) changes in luminescence efficiency. It is however noted that the total number of Si nanocrystals is not increased because the oxidation temperatures, in the range from 600°C to 800°C, are significantly below the as-crystallization temperature ($\geq 1000^\circ\text{C}$). Therefore, since the total number of Si-nanocrystals does not increase by the rapid oxidation, the increasing nc-PL intensity as a function of oxidation temperature (600°C-800°C), shown in Figure 5.2, can only be attributed to the increment of luminescence efficiency. This is in agreement with the fact that at this range of oxidation temperatures, the intensity of defect related PL bands (400 and 515 nm) also decreases, indicating the passivation of oxygen related defects. This can also be related to the oxidation mechanism shown in Figure 5.3(a), in which the non-radiative channels present in the Si-suboxide (SiO_x) encapsulating shells were reduced by oxidation. Nevertheless, it is also possible that the non-radiative channels in the host matrix were passivated by oxygen.

After oxidation at 900°C, however, the monotonous trend of increasing nc-PL intensity in Figure 5.2 is discontinued. Upon oxidation at 900°C, the nc-PL band intensity was reduced significantly and a rise of PL intensity at 530 nm (2.33 eV) was observed. It should be noted that at oxidation temperature of 800°C (below 900°C), defect PL band at 530 nm has been reduced effectively. Therefore, the re-emergence of this PL band upon oxidation at temperature of 900°C can be originated from the defects related to silicon nanocrystals with much reduced average size, ~1 nm. Wolkin et al. [5-10] reported that as the nanocrystal size decreases, the surface effect plays a more prominent role. It is noted that the oxidation temperature of 900°C is well close to the viscoelasticity temperature of SiO₂ (950°C) reported in the literatures [5-1], [5-4], [5-5], leading to a more effective diffusing oxygen to overcome the compressive stress normal to the Si/SiO₂ interface.

5.3.2 Photoluminescence dependence on oxidation time

In Figure 5.2, the oxidation process at temperature of 800°C produces the highest PL intensity and most importantly this temperature is well below the reported viscoelasticity temperature (950°C) [5-4], [5-5]. Based on this result, the temperature of 800°C was chosen to study the PL behaviour as a function of oxidation time. As mentioned in the section 5.3.1 above, the nanocrystal size reduction by oxidation at temperatures below 950°C is still limited by the viscosity of oxide matrix [5-4].

Figures 5.4(a) and 5.4(b) present, respectively, the PL peak energy and peak intensity of sample A, B, and C as a function of oxidation time at 800°C. In Figure 5.4(a), for all samples, a consistent blue-shift of nc-PL peak energy is observed with increasing oxidation time. TEM images in the inset of Figure 5.4(a) show that the Si nanocrystals for the sample oxidized at 800°C for 2 minutes and 10 minutes are 3.2 nm and 2 nm, respectively, indicating that the observed blue-shift of the PL peak is closely related to the reduction of the Si nanocrystals size. In Figure 5.4(a), it is observed that the rate of change of the nc-PL peak position in the first few minutes of oxidation is faster than that in the longer oxidation time. This can be explained as follows. Firstly, after the sample was subjected to process “1” (RTA process in N₂, 1000°C), it was not well-passivated due to such a short/rapid heating and cooling nature of RTA process [5-4]. Secondly, the sample is not fully densified and therefore, the oxygen diffusion to passivate the matrix and reduce the size of Si nanocrystals was very effective in initial stage of rapid oxidation process. In Figure 5.4(a), for sample A, the PL peak energy blue-shift of ~200 meV (~90 nm) in the first 2 minutes of oxidation correlates to a change of average nanocrystals size of about ~0.8 nm. However, in the case of oxidation process from 2 to 10 minutes, the changes of Si nanocrystals size of about ~2 nm corresponds to a PL peak blue-shift of only ~50 meV (19 nm). The relatively more rapid shift of PL peak position in the first 2 minutes could be attributed to the exciton recombination, i.e. quantum confinement effect (QCE). The range of PL peak energy shift agrees well with theoretical and experimental work by Wolkin et al. [5-6]. The relatively much slower peak-shift after oxidation for 2-10 minutes deviates from the quantum confinement prediction [5-6]. This is attributed to the presence of Si=O states on the interface of Si nanocrystals and SiO₂. The rate of PL peak-shift with oxidation time in this work is relatively fast compared to other reported works [5-1], [5-4]. For examples, in order to achieve PL peak-shift of sample A from 780 nm (1.62 eV) to 680 nm (1.82 eV), i.e. a shift of about 100 nm or 0.2 eV, it only requires 10 minutes of oxidation. For comparison, Photopoulos et al. [5-1] reported that oxidation at a single 12 nm Si/SiO₂ bilayer requires relatively long oxidation window, i.e. 120 minutes to engineer the same PL peak shift. Bitten et al [5-7] reported that for oxidation at 800°C for 20 minutes only resulted in a PL peak shift of 80 meV.

(a)

(b)

Figure 5.4 (a) The PL peak energy (eV) of samples A, B, and C as a function of rapid oxidation time. The oxidation temperature is 800°C. (b) The PL peak intensity of samples A, B, and C as a function of rapid oxidation time

In Figure 5.4(b), the PL intensities of sample A, B, and C are presented as a function of rapid oxidation time. Initially, the nc-PL intensity increases to a maximum value before decreases at the longer oxidation time. The increasing nc-PL intensity is attributed to the increase of luminescence efficiency of emitting Si nanocrystals due to defect passivation, i.e. reducing non-radiative decay channels. The optimum nc-PL intensity was observed after oxidation for 4 minutes for sample A and 6 minutes for sample B and C. This indicates that in the samples having relatively thicker SRO layer

(i.e. larger average size of Si-nanocrystals), the non-radiative defect concentration is higher, and thus the required oxidation time to produce the maximum PL intensity is longer. In general, the decreasing nc-PL intensity after achieving the optimum value can be due the following reasons: (i) the number of Si-nanocrystals decreases due to longer oxidation time, (ii) the absorption cross-section of oxidized Si-nanocrystals decreases as the size decreases [5-2], iii) some of the oxidized Si-nanocrystals simply do not give emission, i.e. optically inactive. The first is not likely because the oxidation temperature of 800°C is well below viscoelasticity temperature of 950°C; hence elimination of Si-nanocrystals is rather impossible. Therefore, it is only the second and third reasons which could be used to explain the decrease of nc-PL intensity. In reason (ii) above, the small absorption cross-section of Si nanocrystals with relatively much smaller size occurs due to the decrease of optical density states above the Si nanocrystals related “bandgap” despite the increase in oscillator strength of smaller size due to quantum confinement effect.

5.3.3 Photoluminescence lifetime and uniformity of oxidized samples

In order to understand the nature of radiative emission of this nc-PL band, the lifetime of nc-PL emission were obtained. For the interacting Si-nanocrystals system, the PL lifetime was described by the following relationship [5-2]:

$$I(t) = I_0 \exp\left(-\left(t/\tau\right)^\beta\right) \quad (5.1)$$

in which τ is the effective time constant, and β which is the stretching exponential coefficients and is usually between 0 and 1. $\beta < 1$ implies the interacting Si-nanocrystals system, whereas $\beta = 1$ implies ideally non-interacting Si-nanocrystals system.

Chapter 5

Size Control of Silicon Nanocrystal by Two-step Rapid Annealing Treatment

Figure 5.5 (a) Normalized room-temperature nc-PL decay of as-crystallized and oxidized (at 800°C for 4 and 10 minutes) samples A. (b) nc-PL peak intensity and wavelength for different sample thickness due to etching. Prior to etching process the sample was oxidized at 800°C for 1 minute

Figure 5.5(a) shows the normalized room temperature luminescence decay of samples A: as-crystallized at 1000°C for 2 minutes as well as oxidized at 800°C for 4 and 10 minutes. The luminescence decay traces of all samples were taken at 700 nm. Using the equation 5.1, the author has fitted the experimental data in Figure 5.5(a) and has obtained the relevant parameters β and τ of PL decay profile of samples A. These parameters were presented in Table 5.2.

Treatment for sample A	stretching constant, β	Lifetime, τ
As-crystallized	0.72	35 μs
Oxidized at 800°C for 4 minutes	0.76	46 μs
Oxidized at 800°C for 10 minutes	0.89	57 μs

Table 5.2 Relevant parameters β and τ of nc-PL decay of samples A.

As shown in Table 5.2, the parameters τ and β obtained from the fitting are $\sim 35 \mu\text{s}$ and 0.72 (as-crystallized sample), $\sim 46 \mu\text{s}$ and 0.76 (oxidized for 4 minutes), and $\sim 57 \mu\text{s}$ and 0.89 (oxidized for 10 minutes). This range of lifetimes is comparable with those reported in other literatures for silicon

nanocrystals [5-2], [5-7]. In this work, the values of the experimentally derived parameter constant β are less than 1, demonstrating that the interactions between neighbouring Si-nanocrystals as well as between Si-nanocrystals and defect levels play a prominent part [5-2]. The increasing constant β from 0.76 (as-crystallized) to 0.89 (10 minutes of oxidation) implies that, upon oxidation, the average size of nanocrystals and defect levels are reduced, approaching to an ideal non-interacting light emitting Si-nanocrystals.

The author also investigated the uniformity of oxygen diffusion into the samples. Several 1×1 cm sample cuts from the sample A, which was oxidized at 800°C for 1 minute, were etched using Reactive Ion Etching (RIE) process. The PL spectra for different thicknesses of samples are shown in Figure 5.5(b). The nc-PL intensity at 735 nm (1.69 eV) decreases with increasing etching depth. This is expected because reduction of thickness results in reduction of light emitting Si nanocrystals in the samples. On the other hand, nc-PL peak wavelength remains the same for different thicknesses of sample. This indicates that nanocrystal size reduction occurs quite uniformly throughout the film thickness.

5.4 Photoluminescence enhancement of oxidized samples

The discussion above has shown that a combination of post deposition rapid annealing and oxidation method is a possible and powerful technique developed in this work to engineer Si-nanocrystal size. However, it is known that not all nanocrystals are fully passivated for two possible reasons as follows. Firstly, the short annealing is not enough to form large density of emitting Si-nanocrystals, as evidenced by relatively weak nc-PL intensity prior to hydrogen passivation discussed in section 4.3.4. The presence defect related PL bands also helps explain this argument. Secondly, the short oxidation time is not enough to passivate all defects and improve the luminescence intensity.

Table 5.3 shows three different annealing processes of which the combinations will be carried out and studied for enhancing nc-PL intensity of sample A, B, and C. As shown in Table 5.1, the difference of as-deposited samples A, B, and C is the thickness of SRO layers, with sample C having the largest thickness followed by sample B and then sample A.

Process ID	Annealing type	Annealing Environment	Temperature ($^\circ\text{C}$)	Annealing time (minutes)
Process 1	Rapid thermal annealing (RTA)	N_2	1000°C	2
Process 2	Rapid thermal annealing (RTA)	O_2	800°C	2
Process 3	Furnace annealing	Air	600°C	30

Table 5.3 Different annealing process which will be carried out to study the enhancement of PL intensity of sample A, B, and C

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Three different combination of annealing process described in Table 5.3 were carried out and the resulting nc-PL intensities were studied. The samples treated by process 1 only consists of process 1, which have been termed as “as-crystallized” samples, whereas the samples treated by process 1 and 2 sequentially have been termed as “oxidized” samples. The samples treated by process 1, 2, and 3 sequentially will be termed as “optimized” samples.

Figure 5.6 shows the PL spectra of as-crystallized, oxidized, and optimized sample B. It is observed from Figure 5.6 that the nc-PL intensity of the as-crystallized sample B is indeed much lower than the other two samples (oxidized and optimized samples). Furthermore, the nc-PL peak intensity of optimized sample B is higher by a factor of 3 as compared to the oxidized sample B. Also, it is observed that very little shift of PL peak wavelength of optimized sample B as compared to the oxidized sample. This indicates that further annealing of oxidized samples in 1 atm air at temperature of 600°C (lower than oxidizing temperature of 800°C) for 30 minutes ensures that the in-diffusing oxygen optimized the passivation of oxide matrix or Si-nc/SiO₂ interface defects without severely reducing the Si nanocrystals size.

Figure 5.6 PL spectra of sample B treated with different process combinations: as-crystallized (process 1), oxidized (process 1 and 2), and optimized (process 1, 2, and 3). The normalized nc-PL peak intensity of sample A, B, and C, for different process combinations (inset)

Furthermore, the inset of Figure 5.6 shows the normalized nc-PL intensities of sample A, B, and C for different process combinations (as-crystallized, oxidized, and optimized). It is observed that the normalized nc-PL intensities of oxidized sample A and sample C, respectively, experience the weakest enhancement (by a factor of 2) and the highest enhancement (by a factor of 7) after the annealing in air for 30 minutes. This indicates that a large concentration of defects in sample C has not been passivated during rapid oxidation. This is presumably related to the fact that the as-deposited sample C has the thickest SRO layers and requires higher thermal energy (longer annealing time) to produce well passivated Si nanocrystals upon thermal annealing. However, with only short annealing time of RTA as well as rapid oxidation processes, the concentration of defects remaining in this sample is larger than that in samples A, and B. Therefore, the increment of PL intensity upon long annealing in air for 30 minutes results in much improved nc-PL intensity.

5.5 Summary

In summary, using two-step rapid annealing process on the SRO/SiO₂ superlattice samples, in N₂ and O₂ ambient, sequentially, the author was able to control and improve the PL peak position and intensity. The PL peak wavelength was controlled by reducing the size of nanocrystals using the rapid oxidation process. Simultaneously, oxygen-deficiency related defect has also been reduced effectively by the oxidation process. A less densified SiO₂ host matrix and the low quality of Si-nanocrystal/SiO₂ interface as well as the oxide matrix are the key for the rapid oxidation to control the size. Further annealing in air at 600°C for about 30 minutes improves the oxide matrix and therefore PL intensity without severely reducing the nanocrystals size. These results provide an alternative method to selectively control the PL emission peak via good control of post-deposition annealing temperature, oxidation temperature and short annealing time. Enhancement using annealing in air for 30 minutes at 600°C, which is lower than oxidizing temperature used in the proceeding rapid oxidation process (800°C), has also been presented. The oxidation process method discussed in this chapter is useful for various photonics applications, such as in the optical memory application, and also optical waveguide structure. There is obviously a need to combine the oxidation process with other technique such as mask/pattern to achieve selective oxidation on planar substrates. Several parameters such as structure thickness, sidewall oxidation rate, as well as lateral diffusion of oxygen have to be carefully considered.

Chapter 6

Development of Erbium doped Si-rich Oxide/SiO₂ Superlattice Structures

6.1 Introduction

The Si nanocrystal-related photoluminescence (PL) peak controllability using SRO/SiO₂ superlattice structure was successfully demonstrated and discussed in Chapter 4 and chapter 5. The emission at ~800 nm has been attributed to the quantum confinement effect of Si nanocrystals which were formed by the rapid thermal annealing (RTA) process on the SRO/SiO₂ superlattice samples.

The sensitizing effect of Si nanostructures has been demonstrated to enhance the emission of Erbium (Er) within two or three orders of magnitude as compared to direct excitation of Erbium using the same optical excitation wavelength [6-1]-[6-3]. Now, in this chapter, the development of Si nanostructures as sensitizer for Erbium (Er) emissions is discussed.

Figure 6.1 Schematic of 4f energy levels of Erbium ions in solid [6-4]

Figure 6.1 shows 4f energy levels of Er³⁺ ions in a solid matrix [6-4]. The well known Er emission at 1.55 μm is attributed to the radiative transition from ⁴I_{13/2} to ⁴I_{15/2} in 4f shell of Er ions, which can be optically excited by direct (resonance) optical pumping or indirect energy transfer. The resonance pumping method usually uses wavelengths of 1480 nm, 980 nm, 800 nm, 530 nm, which

correspond to the upward transitions from ground state ($^4I_{15/2}$) to $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, and $^2H_{11/2}$, respectively. Such enhancement of Er emission intensity is largely due to the fact that the absorption cross section of Si is higher than that of Er by five orders of magnitude. Therefore, there is a reasonable expectation that such phenomena can be used to realize the needs for the light source in the optical integrated circuitry or optical interconnection operating at optical communication wavelength (1.55 μ m). For on-chip application, the light emission at 1550 nm (1.55 μ m) is generally desired to maintain the ease of integrating and interfacing with systems operating at the communication wavelength. Furthermore, the well known shielding effect of the 5s and 5p electrons of the host materials on the 4f electrons of Er³⁺ causes the 4f energy levels to be only weakly perturbed by the crystal field of the host materials. This means that the intra-4f electronic transition energies, which are shown in Figure 6.1 below, are nearly independent of the material into which the Er is incorporated.

To date, several works on energy transfer from Si nanostructures to Er³⁺ has been investigated and reported [6-1]-[6-3], [6-5]-[6-11]. In general, there are three important results which can be formulated from various reported works as follows: 1) amorphous Si nanostructures have sensitizing effect as efficient as Si nanocrystals, which means crystallinity is not a requirement for efficient sensitizers [6-5],[6-9], 2) the sensitizing efficiency of Si nanostructure to Er is strongly distance dependent, less than 1 nm [6-10],[6-11], 3) reduction of non-radiative recombination centres which compete with the energy transfer process from Si nanostructure to Er is necessary [6-11], [6-12].

Although a general consensus on the sensitizing effect of Si-nanostructures on Er ions has been established, there are several issues which the author would like to address in this work. In this chapter, the author presents the development of Er:SRO/SiO₂ superlattice structure to investigate several issues which are important for development and optimization of Si-nanostructures as sensitizer for Er, as follows:

1. The effect of Si nanostructure size on the emission of Er has not been clarified due to varying results reported [6-13], [6-14]. The difficulty of studying the dependence of Er emission on Si nanostructure size is due to the fact that in most cases the characterization works were carried out on Er doped bulk Silicon rich oxide (SRO) structure. Therefore, due to the size controllability of Si nanostructures, the author considered superlattice structure of Er:SRO/SiO₂ as a more appropriate approach to investigate the effect of Si nanostructure size on the Er related PL spectra.

2. The high thermal budget annealing treatments (prolonged annealing at high temperature) were usually employed to induce phase separation of Si-rich oxide into Si-nanostructures and SiO₂ phase, crystallize the Si-nanostructures as well as remove the defects [6-15]]. However, it would be more economical if a low thermal budget process such as Rapid thermal annealing (RTA) technique is employed instead of a long thermal annealing. The formation of Si nanostructures (nanocrystals or amorphous nanostructures) using RTA process as well as enhancement by subsequent hydrogen

passivation method have been demonstrated in chapter 4. Therefore, the author considered the implementation of RTA process passivation method to enhance the Er emission.

The contents of this chapter are as follows. In section 6.2, the preparation scheme of Er:SRO/SiO₂ superlattice sample, ranging from film deposition process to post-annealing process are described in detail. The characterization work of Er:SRO/SiO₂ superlattice samples treated by low thermal budget processes (RTA process) and hydrogen passivation method is discussed in section 6.3. In this section, the author will discuss the optimum concentration of Er, the study of annealing and passivation effect on the Er emission, the comparison of Er PL emission spectra of the samples treated by low and high thermal budget processes, as well as size effect of the Si nanostructures on Er emission.

6.2 The Preparation of Er:SRO/SiO₂ superlattice structure

In order to study the enhancement of Er emission at 1.55 μm due to the Si nanostructures, a series of Er:SRO/SiO₂ superlattice samples was prepared and treated using low thermal budget process, i.e. RTA process. Several characterization techniques used will also be presented in this section.

6.2.1 Deposition of Er:SRO/SiO₂ superlattice samples

In this section, the preparation method of the Er:SRO/SiO₂ superlattice samples is described.

Figure 6.2 Cross-section of Er:SRO/SiO₂ superlattice sample

Figure 6.2 shows the cross-section of Er:SRO/SiO₂ superlattice structure developed in this work. The terms “superlattice” refers to the periodical arrangement of Er:SRO and SiO₂ layers. The

periodic Er:SRO and SiO₂ layers are clearly indicated in Figure 6.2. The top SiO₂ buffer was deposited to protect the superlattice structures from oxidation by residual oxygen gas or thermal nitridation during annealing at high temperature in N₂ environment. To deposit the Er:SRO/SiO₂ superlattice samples, the RF co-sputtering technique was used. The objective of doping of Er into SRO layers is to optimize the energy transfer of Si nanostructure to Er, which is strongly distance dependent [6-10], [6-11]. For all deposition process, the sputtering gas was Ar with 6 mTorr partial pressure, and substrate temperature was kept at 100°C. Also, during deposition, the substrate was rotated at (at 20 rpm) to ensure thickness uniformity of the sample. Erbium ions were incorporated into the SRO/SiO₂ superlattice by RF magnetron co-sputtering of three magnetron targets: Erbium oxide (Er₂O₃), Silicon dioxide (SiO₂) and Silicon (Si). During deposition process, the RF power of Si and SiO₂ target were maintained at 80W and 150W, respectively. On the other hand, the RF power of Er₂O₃ target was varied to obtain different concentrations of Er in SRO layers if desired. To deposit SiO₂ layers, only the shutter of SiO₂ target was opened, whereas the shutters of Si and Er₂O₃ targets were closed. When Er:SRO layer was deposited, the shutters of the three targets were all opened.

6.2.2 Annealing methods

To form Si nanostructures (amorphous or crystalline) and to activate Er ions in silica matrix, the rapid annealing method is preferred to avoid clustering of Er which was generally observed at long annealing (furnace annealing) at high temperature [6-15]. Several annealing methods were employed and described as follows:

1. The samples were annealed using the Rapid thermal annealing (RTA) process in N₂ at temperatures, ranging from 500°C to 1000°C, for 2 minutes, to produce Si nanostructures. The RTA steps profile is shown in Figure 6.2. Long thermal annealing was also performed using long quartz tube to study the long thermal annealing effect on non-radiative defect reduction. The long annealing was carried out in flowing N₂ environment at temperatures of 800°C and 900°C for 2 hours. In addition, the annealing time at temperature of 900°C was varied from 30 minutes to 8 hours.

2. A selected group of samples which have been treated by RTA process was annealed in forming gas (FG, 5%H₂:N₂) at temperatures of 500°C to study the effect of passivation on the PL spectra of the Er. The objective of annealing in forming gas was to passivate competing non-radiative recombination centres.

Figure 6.3 Rapid Thermal Annealing (RTA) steps profile

6.2.3 Characterization techniques

The characterization work in this chapter focuses primarily on Photoluminescence (PL) measurement technique which was performed by pumping with 442 nm line of He-Cd laser with a power of 20 mW. The spectral data were recorded with a lock-in amplifier as a reference. The PL set up was discussed in more detail in Chapter 3 section 3.2.1.4.2. All PL measurements were performed in room temperature. To study the structural behaviour of the superlattice upon RTA treatment, two other characterization techniques were used. They are Fourier transform infrared (FTIR) spectroscopy and transmission electron microscopy (TEM) techniques which have respectively been described in detail in Chapter 3 sections 3.2.1.2 and 3.2.2.1.

6.3 Characterization results of Er:SRO/SiO₂ superlattice samples

The discussion in this section consists of the following: (i) the study of the optimum Er concentration, (ii) the study of the structural evolution in the samples due to rapid thermal annealing (RTA) process, (iii) the effect of passivation on the Er emission (iv) comparison of low thermal budget process used in this work (RTA and passivation methods) with long annealing process, and lastly, (v) the size effect of Si nanostructures on Er emission.

6.3.1 The Optimum Erbium concentration

In order to optimize the Erbium concentration, a series of Er:SRO/SiO₂ superlattice samples with different concentrations of Er were prepared.

Sample ID	Er concentration (at.%)	Thickness of Er:SRO layer	Thickness of SiO ₂ layer (nm)	Number of Er:SRO/SiO ₂ layers
Er1	1	N/A	200	1
Er2	0.9	3	5	32
Er3	2	3	5	32
Er4	2.6	3	5	32
Er5	4	3	5	32
Er6	1.2	3	5	32

Table 6.1 The physical dimension of cross-section structures of sample Er1 (bulk Er:SiO₂) and samples Er2 to Er6 (Er:SRO/SiO₂ superlattice) as well as the Er concentration in each sample.

Table 6.1 presents the thicknesses of Er:SRO and SiO₂ layers, the Er concentrations in Er:SRO layers, and the numbers of periodic layers (Er:SRO and SiO₂ layers) of samples Er2-Er6. The similar details of sample Er1, which is Er:SiO₂ (without excess Si), is also included. The number of periodical layers (Er:SRO and SiO₂ layers) of each sample was 32. The total thickness of each sample was ~300 nm. As shown in Figure 6.2, a 20 nm thick SiO₂ top buffer was deposited for each sample to reduce residual oxygen diffusion as well as thermal nitridation during annealing in N₂ environment. In Table 6.1, it is shown that samples Er2 to Er6 have the same thicknesses of Er:SRO and SiO₂ layers but different Er concentrations, ranging from 0.9 at.% to 4 at.%. Sample Er1, which is a simple Er:SRO bulk was also deposited and treated for comparison.

Figure 6.4 Er-PL spectra of Er:SRO/SiO₂ superlattice samples Er2 (0.9 at.% Er:SRO), Er3 (2 at.%), Er4 (2.6 at.% Er), Er5 (4 at.% Er), and Er6 (1.2 at.% Er) after RTA process in N₂ ambient at 850°C for 2 minutes. The excitation wavelength used is 442 nm.

Figure 6.4 shows the Er-PL spectra for Er:SRO/SiO₂ superlattice samples Er2 to Er6, which have different Er concentration in SRO layers, after being treated by RTA process in N₂ environment for 2 minutes at optimum temperature of 850°C. When optically excited using the 442 nm He-Cd laser line, the Er-PL spectra peaked at 1.53 μm of the Er:SRO/SiO₂ superlattice samples are observed. However, there is no Er-PL band observed from sample Er1 (a 1.2 at.% Er doped SiO₂ without Si nanostructure), indicating that the emitting Er ions are only those excited via a non-radiative energy transfer mechanism. It is also observed from Figure 6.4 that the Er-PL intensity also changes with different concentration of Er in the SRO layers. The PL intensity increases as the Er concentration increases from 0.9 at.% to 1.2 at.% and then decreases as the Er concentration increases to 4 at.%. The increase of Er-PL as the Er concentration increases to ~1.2 at.% can be related to the increase of optically active Er. On the other hand, the decrease of Er-PL intensity as the concentration increases further to 4 at.% can be attributed to the clustering of Er atoms which is commonly observed after annealing at high temperature [6-1]-[6-3],[6-15]. The phenomena of PL quenching at relatively high Er concentration is generally known as “Er concentration quenching” [6-16]. On the basis of this result, in all of the following discussions, the author focuses only 1.2 at.% Er:SRO/SiO₂ superlattice samples. A more detailed study on the effect of RTA process on Er emission will be discussed in section 6.3.3.

6.3.2 Structural evolution due to rapid thermal annealing

It is known that annealing especially at high temperatures can induce structural changes, especially for non-stoichiometric samples such as the samples prepared in this work.

Figure 6.5 FTIR absorption spectra (1350-400 cm⁻¹) of sample Er6 treated with different RTA temperatures: 500°C, 600°C, 800°C, 900°C and 1000°C.

Figure 6.5 shows the FTIR absorption spectra of the sample Er6 for different RTA temperatures. The sample Er6 exhibits the highest Er emission upon RTA in N₂ at 850°C for 2 minutes. Upon RTA process at different temperatures, changes in the prominent absorption bands, namely the Si-O-Si stretching (1053-1075 cm⁻¹) and Si-O-Si asymmetric stretching band (1145 cm⁻¹), are observed. The shift of Si-O-Si stretching absorption peak from 1053 cm⁻¹ to 1075 cm⁻¹ with increasing RTA temperature from the as-deposited to 1000°C is related to the restructuring of the network closer towards SiO₂ phase. The thermally grown SiO₂ sample has Si-O-Si stretching band peaked at ~1080 cm⁻¹. Since the as-deposited samples has large excess Si in the SRO layer, such evolution towards SiO₂ phase indicates the formation of Si clusters. The absorption band at 1145 cm⁻¹ becomes less distinctive as annealing temperature increases to about 900°C and 1000°C, because it overlaps with the Si-O-Si stretching band which shifts towards higher wavenumbers with the increase of annealing temperature. Gourbilleau et al. [6-17] reported in the work on bulk Si-rich oxide sample that the increase of relative intensity of the longitudinal optical (LO₃) mode (1250 cm⁻¹) for the Si-O vibrational mode with respect to the transversal optic (TO₃) mode (~1080 cm⁻¹) can be related to the increase of the interfacial silica, i.e. Si/SiO₂ interface, which indicate the increase of amorphous Si

nanostructures. However, such change is not observed in Figure 6.5. This is presumably due to the fact that the samples studied in this work are SRO/SiO₂ superlattice structures. The density of such interface of Si nanostructures in the annealed sample Er6 is not as high as that of annealed bulk Si-rich oxide and therefore the signals related two bands LO₃ and TO₃ are not detectable by FTIR spectroscopy.

Figure 6.6 TEM images of sample Er6 after RTA process in N₂ environment at various temperatures showing (a) distinctive alternate layers indicating the superlattice structure (b) absence of Si nanostructures after rapid thermal annealed at 700°C, (c) amorphous Si nanostructures with absence of lattice fringes after rapid thermal annealed at 850°C, (d) Si nanostructures, which are possibly mixtures of crystalline and amorphous Si nanostructures after rapid thermal annealed at 1000°C.

TEM characterization of sample Er6 has been carried out and the images are shown in Figure 6.6, which consists of: (a) distinctive alternate layers indicating superlattice structure of Er:SRO

(darker layers) and SiO₂ (brighter layers), (b) absence of Si nanostructures after rapid thermal annealed at 700°C, (c) amorphous Si nanostructures with absence of lattice fringes after rapid thermal annealed at 850°C, (d) Si nanostructures, which are possibly mixtures of crystalline and amorphous Si nanostructures after rapid thermal annealed at 1000°C.

The evolution of IR absorption band with RTA temperature in Figure 6.5 can also be correlated with the transmission electron microscopy (TEM) images of sample Er6 shown in Figure 6.6. Figure 6.6(b) and 6.6(c) show, respectively, the absence of Si clusters after rapid annealing at 700°C and the presence of amorphous Si nanostructures with the absence of lattice fringes after RTA temperature of 850°C. In Figure 6.5, a small absorption band from 620 to 730 cm⁻¹ is also observed. This absorption band exists in the as-deposited samples and even in the samples annealed at 1000°C. This is usually attributed to oxygen deficiency centres [6-18], which could be in the form of Si-Si clusters or H-terminated bonds. In Figure 6.5, after RTA process at 1000°C, the Si-O-Si stretching absorption peak is at 1075 cm⁻¹, which is very close to 1080 cm⁻¹ (the Si-O-Si stretching absorption peak of SiO₂ material). In Figure 6.6(d), it is also shown that most of Si nanocrystals only occur after RTA process at 1000°C. These two complimentary evidences indicate that after RTA process at 1000°C, a clear phase separation of Si-rich oxide into Si and SiO₂ occurs.

6.3.3 The effect of passivation on Erbium emission

The study on the Er-PL intensity of the samples is presented in this section. The behaviour of Er PL peak intensity of the samples which were treated by RTA process with and without subsequent passivation in FG is discussed.

Sample ID	Er concentration (at.%)	Thickness of Er:SRO layer	Thickness of SiO ₂ layer	Number of multilayer
Er6	1.2 at.%	3 nm	5 nm	32
Er7	1.2 at.%	1.5 nm	5 nm	32
Er8	1.2 at.%	2 nm	5 nm	32
Er9	1.2 at.%	3.7 nm	5 nm	32
Er10	1.2 at.%	4.5 nm	5 nm	32
Er11	1.2 at.%	6 nm	5 nm	32

Table 6.2 The deposition parameters and cross-section structure of Er:SRO/SiO₂ superlattice samples Er6 to Er11.

Table 6.2 presents the thicknesses of Er:SRO and SiO₂ layers in, the Er concentration in the SRO layer of, and the number of periodic layers of samples Er6 to Er11. From table 6.2, it is shown that for samples Er6 to Er11, Er concentration is maintained at 1.2 at.%, while the thickness of Er:SRO layer is varied.

Figure 6.7 (a) visible PL spectra and (b) Er-PL spectra of sample Er6 for different RTA temperatures.

Figure 6.7(a) and 6.7(b) show Si-nanocrystal and Er-PL spectra of sample Er6 treated with RTA only, which has SRO layer thickness of 3 nm. In Figure 6.7(b), it is observed that the Er-PL intensity increases as the RTA temperature increases from 500°C to an optimum temperature at 850°C. However, the intensity decreases at higher RTA temperature and becomes relatively very weak after annealing at 1000°C. While the Er-PL emission in the IR wavelength range varies with RTA process temperature (see Figure 6.7 (b)), the PL bands in visible range (see Figure 6.7(a)) are very weak to give useful data. In fact, even after annealing at 1000°C, there is only a small PL intensity at 810 nm observed. This PL intensity is related to Si nanostructures. It is generally known that rapid annealing, especially at high temperatures, such as ~1000°C, can induce clustering of Si atoms, but unavoidably leaves large concentration of defects, which could be radiative or non-radiative trapping centres. The weak intensities of Si-nanostructure related PL and Er-related PL can either be due to the inefficient energy transfer because of the large non-radiative defects on the Si-nanostructure/SiO₂ interface or energy migration from Er to nearby defect states with energies in the IR range. It is therefore necessary to carry out annealing in FG at lower temperature (500°C) to study the effect of passivation on the Er-PL intensity.

Figure 6.8 Er-PL peak intensity at 1.53 μm of Er:SRO/SiO₂ superlattice samples as a function of RTA temperature (a) without and (b) with subsequent annealing in FG. Each trend represents the Er-PL intensity of superlattice samples (Er6 to Er11)

Figure 6.8(a) and 6.8(b) show the behaviour of Er-PL peak intensity at 1.53 μm of the superlattice samples (Er6 to Er11) with different thickness of Er:SRO layers as a function of RTA temperature before and after passivation in FG, respectively. In Figure 6.8(a), the Er-PL peak intensity is almost constant with increasing annealing temperature from 500°C to 700°C. On the other hand, a different behaviour of Er-PL peak intensity after passivation in FG (5% H₂: N₂) at 500°C for 1 hour is observed in Figure 6.8(b). For samples treated by RTA process at temperatures of 700°C or below prior to passivation, almost no Er-PL intensity is observed. This means that Er-PL intensity is effectively quenched by annealing in FG.

From the discussion in Chapter 4 section 4.3.4, it has been concluded that the use of annealing in forming gas (FG) is to passivate competing non-radiative recombination centres on the surface or surrounding of Si-nanostructures which still exist due to short annealing time. In Chapter 4, the author has demonstrated that by the same annealing treatment in FG, the non-radiative recombination centres has been reduced, supported by the increase of Si nanostructures related emission by a factor of ~ 8 .

Transmission electron microscopy (TEM) characterization result in Figure 6.6(b) also reveals the absence of Si clustering in the samples annealed at RTA temperature of 700°C. However, it is also

possible that the Si clustering has already occurs at temperature as low as 700°C but undetected by the TEM because of its very small size. A clear clustering of Si is only observed after RTA temperature at 850°C, as indicated in Figure 6.6(c). Nevertheless, since the author observes the quenching instead of the expected enhancement of Er emission due to passivation, it is sufficient to suggest that the Er emission of the samples treated by RTA at temperature of 700°C or below sensitized is through defect mediated energy transfer rather than energy transfer from Si nanostructure.

For the unpassivated samples in Figure 6.8(a), the optimum Er-PL peak intensity is observed at RTA temperature of 850°C before it begins to decrease at higher RTA temperature. To understand the energy transfer mechanism to Er emission, passivation effect on the Er emission of samples rapid annealed at temperatures of 850°C and above must be studied.

In Figure 6.8(b), after passivation in FG, the peak Er-PL intensity begins to increase with increasing RTA temperature, ranging from 700°C to 1000°C. For all samples, a large increase of PL intensity from RTA temperature of 850°C to 1000°C is observed. It is also noted that TEM images in Figures 6.6(c) and 6.6(d) show the presence of amorphous Si nanostructures (~2 nm size) and Si nanocrystals (~3 nm size) in sample Er6 after RTA process at 850°C and 1000°C, respectively. Such an increase of Er-PL peak intensity can therefore be related to the passivation of non-radiative recombination centres (defects) at IR energy levels which compete with the energy transfer from Si nanostructures. It is also necessary to state that after rapid annealing at 1000°C, not all Si nanostructures are crystallized due to short annealing time (~2 minutes) and temperature lower than 1100°C-1200°C. Rather, a mixture of amorphous Si nanostructures and nanocrystals is present in the sample. However this is not a critical issue because amorphous Si nanostructure is as good an Er sensitizer as its nanocrystal counterpart. Er-PL peak intensities of samples Er6 to Er10 (see Table 6.2) passivated in 5%H₂:N₂ at 500°C for 1 hour, follow a similar increasing trend with increasing RTA temperature. On the other hand, the Er-PL peak intensity of sample Er11 (SRO thickness of 6 nm) begins to increase quite significantly after RTA process at 800°C, well below the temperature of 900°C required for other samples. Comparing the Er-PL intensities of all samples after rapid annealed at the same temperatures in the range of 800°C to 1000°C, it is concluded that passivation is necessary to induce the effective emission of Er through Si nanoclusters/nanocrystals mediated energy transfer by passivating the non-radiative recombination centers, such as Pb-defect centres, i.e. Si-dangling bonds on the surface of Si nanostructures [6-19] and defects with energies in IR wavelength range, which effectively capture the excitons.

6.3.4 The comparison of Erbium emission by rapid and long thermal annealing

In this section, the effectiveness of the low thermal budget RTA process and passivation as an alternative to long furnace annealing (FA) process is presented. Figure 6.9 shows the Er-PL spectra of the samples Er6 treated using the RTA process and furnace annealing. It is found that Er-PL peak intensity at 1.53 μm of sample Er6 annealed at 1000°C for 2 minutes and followed by hydrogen passivation is comparable with that of sample Er6 annealed in furnace annealing in N₂ environment for long period of 8 hours. A combination of short time annealing at the onset of crystallization of Si nanostructures and passivation is more effective to reduce non-radiative recombination centres than long furnace annealing. For a complete study, lifetime study of Er emission at 1.53 μm is necessary to understand the environment of Er after RTA process and long furnace annealing. However, this is beyond the scope of this work.

Figure 6.9 Er-PL spectra of samples annealed by RTA and long furnace annealing (FA)

Long furnace annealing at 1000°C or higher temperature will cause precipitation of the Er in silica matrix. The onset temperature for Er-clustering in SiO₂ is well known to be at ~900°C [6-14]

6.3.5 The size effect of Si nanostructures on Erbium emission

The effect of Si nanostructure size on Er peak emission intensity is shown in Figure 6.10. The Er-PL spectra were taken from the samples Er6 to Er11, which have corresponding Er:SRO layer thickness of 1.5 to 6 nm, after RTA process in N₂ at 1000°C for 2 minutes followed by the hydrogen

passivation. At first, the Er-PL peak intensity increases as the SRO layer thickness increases from 1.5 nm to 3 nm. For sample with SRO layer thickness of 1.5 nm and 2 nm, the rapid thermal annealing will induce very small Si nanostructures, which is very difficult to observe using the Transmission Electron Microscopy (TEM). It is believed however that the density of Si nanostructures from such a thin SRO layers is not large and that upon annealing, the Si-rich oxide layer is highly strained and defective. It is also reported by Bongersma et al. [6-20] that the absorption cross section of much smaller Si nanocrystals (emitting at wavelength shorter than 700 nm) decreases with decreasing nanocrystals size. As the nanostructure size decreases, the energy bands become more discontinued, and therefore the effective absorption cross section is reduced.

Figure 6.10 Er PL peak intensity at 1.53 μm as a function of the SRO layer thickness

On the other hand a consistent decrease of Er-PL intensity is observed for samples with SRO layer thickness larger than 3 nm. This can be related to three possible causes:

1. As the SRO layer thickness increases, Si nanostructure size increases in size. When the Si nanostructure size is comparable or larger than exciton Bohr radius in Si, ~ 5 nm, the confinement effect becomes weakened. When optically excited, an exciton pair is generated in core of Si nanostructures and then recombines on the surface of the nanostructures. Such exciton confinement effect is only strongly demonstrated by Si nanostructure with size smaller than 5 nm [6-14]. For nanostructure size larger than ~ 5 nm, a weak confinement and shrinkage of band gap can reduce the efficiency of energy transfer to the upper excited levels of Er.

2. The possibility of deexcitation process, such as energy back-transfer and Auger type interaction between Er and excitons become increasingly larger with increasing Si nanostructures because of the shrinkage of bandgap [6-21] and larger surface area of nanostructures.

3. Or simply, the surface of large Si clusters (>5 nm) are more defective and it requires longer passivation time or higher passivation temperature to reduce the dangling bond effectively and improve the energy transfer to Er.

6.4 Summary

The Er:SRO/SiO₂ superlattice samples prepared using the RF magnetron co-sputtering process with three magnetron targets: Si, SiO₂, and Er₂O₃ has been successfully fabricated. The as-deposited samples were treated by using the rapid thermal annealing (RTA) process in N₂ environment at temperatures of 500°C to 1000°C for 2 minutes. The effects of annealing RTA temperature without passivation are as follows. After rapid annealing at temperatures of 700°C or below, the indirect excitation of Er is dominated by defect-mediated energy transfer mechanism. At 850°C, contribution of Si nanostructures for energy transfer is more significant. However, with increasing RTA temperature, large concentration of defects which act as non-radiative recombination centres, also increases. This is attributed to the rapid heating and cooling in RTA process.

After annealing in forming gas (5%H₂:N₂) termed as hydrogen passivation, the defects responsible for energy transfer in the samples rapid annealed at 700°C or below are passivated, resulting in quenching of Er-PL intensity again, as shown in Figure 6.8(a). On the other hand, for samples rapid annealed at temperature of 800°C to 1000°C, passivation is important to reduce the competing non-radiative recombination centers for efficient energy transfer from Si nanostructures to Er ions. Lastly, the optimum Er emission in the developed samples is observed for sample Er6, which has Si nanostructures size of 3.5 nm. The effect of Si nanostructure size on Er emission has also been discussed and possible explanation has been discussed in section 6.3.5.

Chapter 7

Light Enhancement using Two-Dimensional Photonic Crystal Slab Structures

7.1 Introduction

The author has presented and discussed the photoluminescence (PL) of SRO/SiO₂ and Er:SRO/SiO₂ superlattice in Chapters 4 and 6, respectively. In Chapter 5, the author has also presented and discussed the size control of the Si nanocrystals using oxidation method. In the chapter 4 and 6, the author has demonstrated the use of annealing in forming gas (FG) with gas composition of 5%H₂ and 95%N₂ (5%H₂:N₂) to enhance, respectively, the light emission from Si nanostructures and energy transfer to Er ions by hydrogen passivation of defects. Indeed, the PL intensity of Si nanostructures increases by a factor of 8 as compared to that of the rapid annealed sample without further annealing in FG. Upon annealing in FG at 500°C, the Er emission peaked at 1.53 μm is enhanced largely due to more efficient energy transfer from Si nanostructures to Er ions by hydrogen passivation of competing non-radiative recombination centres.

Generally, in simple light emitting uniform slab structures with effective refractive index, $n_g = n / n_{air}$, it is estimated that only $\sim 1/(4n_g^2)$ of the light emitted is radiated out through the top or bottom [7-1], whereas the rest of the light simply remain trapped in the slab film through total internal reflection (TIR). This results in a low light output efficiency of light emitting layer especially for those with high refractive indices.

In the recent years, two-dimensional photonic crystals (2D PC) slab structure has a potential for enhancing the extraction of light in the vertical direction from a light emitting layer [7-2]-[7-7]. In this work, the interest is to enhance the light output efficiency from a light emitting layer. Enhancement of light output by PC structure can be related to the inhibition of light trapping in the guided modes by coupling to leaky resonant modes and/or photonic band gap mode [7-8]. In addition, a thin slab two-dimensional (2D) photonic crystal can also produce a direct enhancement of the spontaneous emission process by quantum electrodynamics effects (QDE), which occurs through the modification of the optical mode density, and the concentration of electric field fluctuations within the photonic crystal (PC) region.

In this chapter, the author presents the work on the implementation of PC patterns penetrating the Si-rich oxide/SiO₂ and Er:Si-rich oxide/SiO₂ superlattice structures to improve the light output efficiency at visible (600-900 nm) and IR (1550 nm). In principal, this penetrating PC structure is more capable of manipulating the light compared with the typical structure having separated emitting layer and PC structure (extraction) regions.

7.2 The preparation of SRO/SiO₂ and Er:SRO/SiO₂ 2D superlattice based photonic crystal slab structures

Figure 7.1(a) shows a schematic of Si-rich oxide/Silica (SRO/SiO₂) and Er doped Si-rich oxide/Silica (Er:SRO/SiO₂) superlattice samples. The SRO/SiO₂ and Er:SRO/SiO₂ superlattice structures were deposited by RF co-sputtering method on Si substrates with 100 nm SiO₂ buffer layer on top. The deposition procedures for SRO/SiO₂ and Er:SRO/SiO₂ superlattice samples have been described in Chapter 4 and 6, respectively. However, the total thicknesses of all superlattice samples in this work were kept at around 240 nm. A 40 nm thick SiO₂ layer was deposited on top of the superlattice layers.

Prior to the fabrication of PC slab structures, the as-deposited samples were annealed by the rapid thermal annealing (RTA) process. The SRO/SiO₂ superlattice based sample were treated by the RTA process in N₂ environment at 1000°C for 10 minutes, whereas the Er:SRO/SiO₂ superlattice based samples were treated by RTA process in N₂ environment at 1000°C, for 2 minutes. The two different superlattice samples were then annealed in forming gas (5%H₂:N₂) at 500°C for 1 hour to passivate the defects in the samples.

To investigate the enhancement of radiated emission, the PC slab structures were designed and fabricated. Figure 7.1(b) shows the schematic of SRO/SiO₂ and Er:SRO/SiO₂ superlattice based photonic crystal (PC) slab, respectively. In Figure 7.1(b), the label 1 and 2 indicate the air hole and solid dielectric regions, respectively. Figure 7.1(c) shows the image of triangular lattice of air hole PC slab structure taken by scanning electron microscopy (SEM) technique. The labels a , r , and h , in Figure 7.1(b) and 7.1(c) refer to lattice constant, air hole radius, and etch depth, respectively.

The triangular lattice air-hole PC slab structures in all samples were fabricated by deep-UV etching process of the upper cladding down through almost entire active region (SRO/SiO₂ and Er:SRO/SiO₂ superlattice structures) with the etching depth of $h=300$ nm. The 248 nm deep UV lithography was used for patterning PC structure. In the process, the dose and focus value was set for targeting one dimension hole size. The dry etch was processed in Applied Material P5000 etcher

chamber, the etch end point process was used for controlling the etch depth. The post PRS wet cleaning was processed by HF:DI water (1:200) for 10 seconds and H_2SO_4 for 10 minutes.

Figure 7.1 Schematic of (a) SRO/ SiO_2 or Er:SRO/ SiO_2 superlattice samples and (b) side view of SRO/ SiO_2 or Er:SRO/ SiO_2 superlattice 2D photonic crystal slab structure, The label 1 and 2 indicated in (b) refer to air and solid material, respectively. (c) the image of 2D PC pattern fabricated in this work. The labels indicating lattice constant (a), air hole radius (r), and slab thickness (h) are shown (b) and (c)

7.3 Enhancement of photoluminescence of SRO/SiO₂ based photonic crystal slab

Two important parameters of 2D PC pattern to be investigated in this work are: (i) lattice constant (a), which was defined as the periodical distance between the centres of adjacent air holes (see Figure 7.1(c)), and (ii) duty cycle ($\rho=r/a$), which is defined as the ratio of the air hole radius and lattice constant.

Pattern ID	Lattice constant, a (nm)	Air hole radius, r (nm)		Duty Cycle ($\rho=r/a$)
		Designed	Fabricated	
B2	400	110	123.3	0.308
C6	400	115	130.7	0.327
B1	400	120	145.1	0.363
C1	400	130	167.7	0.419
D4	500	150	143.9	0.373
E9	700	180	226.9	0.3106
F9	700	200	217.5	0.346
F8	700	220	242.1	0.39
F6	700	260	271.9	0.47

Table 7.1 The physical dimensions of lattice constants, air hole radii (r), and duty cycles of the SRO/SiO₂ superlattice based 2D PC patterns

Several different patterns of SRO/SiO₂ superlattice based 2D PC patterns with various lattice constants and duty cycles have been fabricated and presented in Table 7.1. The physical dimensions of all 2D PC patterns shown on Table 7.1 were obtained using Critical Dimension Scanning Electron Microscopy (CD-SEM) to ensure correct dimension of the lattice constant and hole radius. It is also observed from Table 7.1 that the fabricated air hole radii are different from design radii. This is because during the lithography process, the alignment was focused on one design air hole radius only, making other fabricated air hole radii to drift from the design ones.

The Photoluminescence (PL) spectra of the 2D PC patterns were collected vertically (normal to the sample surface) at room temperature (25°C) by Micro Raman PL system with excitation source of 488 nm and incident power of 3 mW. The Micro Raman PL system used here has been described in more detail in Chapter 3 section 3.2.1.4.3. The recorded PL intensities were normalized to the effective area of the active material, $(1 - \frac{2\pi\rho^2}{\sqrt{3}})$ for each pattern. The PL spectrum of the unpatterned region (simple slab region) was also measured for comparison.

Figure 7.2 (a) Recorded and (b) normalized PL intensity of un-patterned and patterned samples B1 ($a=400$ nm, $\rho=0.363$), D4 ($a=500$ nm, $\rho=0.373$), F8 ($a=700$ nm, $\rho=0.39$)

Figure 7.2(a) and 7.2(b) show the recorded and normalized PL spectra, respectively, of the un-patterned and patterned samples B1 ($a=400$ nm, $\rho=0.363$), D4 ($a=500$ nm, $\rho=0.373$), F8 ($a=700$ nm, $\rho=0.39$). The duty cycles of the PC patterns are almost constant and only the lattice constants which are widely varied. The PL spectrum of un-patterned region has peak wavelength at 740 nm. From Figure 7.2(b), it is observed that the PL spectra of the patterned regions are dependent on the lattice constant. For a given duty cycle, the PL intensity increases with the increase of lattice constant. The strongest enhancement of PL intensity by four-folds is observed for pattern F8 as compared to that of the un-patterned region.

To explain the effect of the PC structures on the enhancement observed in Figure 7.2(b), the author used the theoretical approach based on the photonic band structure modulation of 2D PC slabs.

Figure 7.3 The photonic band diagrams for Photonic Crystal (PC) slab with pattern for duty cycle ($\rho=r/a$) of (a) 0.3 and (b) 0.4, respectively

Figures 7.3(a) and 7.3(b) show the photonic band diagrams of PC slabs for sample with duty cycles (ρ) of 0.3 and 0.4, respectively. This photonic band diagram was simulated using commercial software BandSOLVE developed by RSOFT Design group [7-9]. Several important parameters such as refractive index of the material, the air hole radii, and the lattice constants are necessary. For measurement of refractive index, the 1 μm thick SRO/SiO₂ superlattice structure (without 2D PC pattern) were prepared with the process parameters similar to the sample patterned with 2D PC. Using prism coupling technique, the refractive index of the materials was measured to be ~ 1.65 at 632 nm.

In Figure 7.3, the photonic band diagram consists of (i) a light cone which is the above the light line of air (black solid line), (ii) the transverse electric (TE)-like modes (blue dotted lines) and transverse magnetic (TM)-like modes (red dotted lines) and (iii) a photonic bandgap (PBG) region defined by the shaded rectangular-shaped region. The modes above the light line of air are radiation modes, which are inherently leaky and extended infinitely to the free-space outside the PC slab structure. On the other hand, the modes below the light line of air are the guided modes, which is actually the eigenmodes of the PC slab. These guided modes are allowed to propagate along the horizontal plane with intensity exponentially decaying into the free-space. However, there is a shaded rectangular region called the PBG region, in which no propagation modes are allowed. Principally, the

PBG region is created as a result of multiple Bragg scattering of photons by lattices of periodically varying refractive indices [7-10], [7-11].

In Figure 7.2, the PL peak intensity of sample F8 ($a=700$ nm, $\rho=0.39$) is higher by factors of 1.3 and 1.5 than those of sample D4 ($a=500$ nm, $\rho=0.373$) and sample B1 ($a=400$ nm, $\rho=0.363$), respectively. According to the Figure 7.3(b), the PL peak of sample F8 at 700 nm corresponds to normalized frequency (a/λ) of ~ 1 , which is near the Γ point of the TE-like leaky modes (indicated by arrow). Likewise, the PL peak of pattern D4 ($a=500$ nm, $\rho=0.373$) at 724 nm, corresponds to normalized frequency (a/λ) of ~ 0.69 , which falls just above the light line of air ($a/\lambda=0.66$). On the other hand, the PL peak of pattern B1 at 740 nm corresponds to normalized frequency (a/λ) of ~ 0.54 , which falls below the light air line and just outside the PBG region. Therefore, the increasing PL intensity with increasing lattice constants is because the generated light strongly couples with the high-Q quality factor leaky modes which eventually escape to free space from the slab in vertical direction [7-2].

Figure 7.4 The scanning electron microscopy (SEM) image of the PC pattern with targeted parameters: (a) $a=400$ nm, $r=120$ nm, $\rho=0.3$, (b) $a=350$ nm, $r=110$ nm, $\rho=0.3$ (bad patterning result).

Several other patterns with smaller lattice constants, such as 350 nm, were also fabricated. However, the PC patterns were not well fabricated. Although the lattice constant of 350 nm can be easily made, if the size of the sizes (diameters) of air holes are too close to the lattice constants causing the air holes structures starts to be interconnected to each other, thus resulting in an unusable PC slab structures. Two images of fabricated 2D PC patterns in this work are shown in Figure 7.4 and can be used to illustrate the fabrication problem. In Figure 7.4(a), the 2D PC pattern with lattice constant (a) of 400 nm and duty cycle (ρ) of 0.3 is well fabricated. However, in Figure 7.4(b), with

lattice constant (a) decreases to 350 nm and duty cycle (ρ) maintained at 0.3, the air hole structure cannot be well fabricated. In this work, the effects of duty cycle on the PL emission enhancement were also studied by comparing the PL spectra of the patterns with the same lattice constants but different sizes of air hole.

Figure 7.5 PL spectra of SRO/SiO₂ superlattice based photonic crystal slab sample annealed in N₂ at 1000°C for 10 minutes

Figure 7.5 shows the PL spectra of un-patterned and patterns: E9, F9, F8, F6 which have the same lattice constant of 700 nm but different duty cycles of 0.31, 0.34, 0.39, and 0.47, respectively. It is observed that the increase of air hole size or duty cycle from 0.31 to 0.47 results in blue-shift of PL peak from 730 nm to 705 nm, respectively. That is because when the air hole size (volume) increases, while maintaining the lattice constant and the slab depth constant, the effective refractive index of the PC slab structure decreases, thus resulting in the blue-shift of photonic band structures. This effect is illustrated by Figure 7.6, which shows the calculated photonic band diagrams of PC patterns E9 ($\rho=0.31$), F9 ($\rho=0.346$), F8 ($\rho=0.39$), and F6 ($\rho=0.47$). Indeed, the PBG region is lifted up from $\rho=0.31$ to $\rho=0.39$. It is however observed that there is no PBG region in the guided modes for pattern F6 ($\rho=0.47$).

Figure 7.5(a) shows that the recorded PL intensity decreases with increasing air hole radius. The strongest PL intensity is recorded for pattern E9 ($\rho=0.31$) whereas the lowest PL intensity

belongs to pattern F6 ($\rho=0.47$). However, the PL intensity of sample F6 ($\rho=0.47$) is reduced below the that of un-patterned sample. The possible reason for such reduction is explained as follows. It is understood that the PL enhancement is greatly influenced by high Q-leaky resonant effect rather than the PBG effect. Therefore, the absence of PBG could not be used to explain the weaker PL intensity of sample F6 ($\rho=0.47$). On the other hand, in Figure 7.6(d), a portion of the modes/states lying around K point (indicated by arrow) is almost lifted up above the light line of air for pattern F6 ($\rho=0.47$), which implies that more radiation modes should be available for pattern F6 ($\rho=0.47$) than for other patterns with smaller duty cycles (E9 ($\rho=0.31$), F9 ($\rho=0.35$), and F8 ($\rho=0.39$)). Therefore the conflicting theoretical and experimental result of PL spectra of sample F6 is most possibly related to the quality of the fabricated pattern. The duty cycle (ρ) of sample F6 is 0.47, which implies a very thin wall between air holes ($700 \text{ nm} - 2 \times (0.47 \times 700 \text{ nm}) = 42 \text{ nm}$). Such a small dielectric region air holes might not be well fabricated.

Figure 7.6 Calculated photonic band diagrams of PC patterns E9 ($a=700$ nm, $\rho=0.31$), F9 ($a=700$ nm, $\rho=0.35$), F8 ($a=700$ nm, $\rho=0.39$), and F6 ($a=700$ nm, $\rho=0.47$).

7.4 Enhancement of photoluminescence of Er:SRO/SiO₂ based photonic crystal slab

In this section, the author also carried out the study of the effects of Photonic crystal (PC) on the enhancement of infrared (IR) PL spectra from Si-nanostructure sensitized Er embedded SiO₂. The physical dimensions of the lattice constants, air hole radii and the duty cycles of Er:SRO/SiO₂ superlattice based photonic crystal (PC) patterns are listed in Table 7.2 below.

Pattern ID	Lattice constant, a (nm)	Air hole radius, r (nm)	Duty Cycle ($\rho=r/a$)
Y5	800	298	0.37
Z5	1000	337	0.34
Z8	1500	444	0.29
Z2	1500	627	0.42

Table 7.2 The physical dimensions of lattice constants, air hole radii (r), and duty cycles of Er:SRO/SiO₂ superlattice based photonic crystal (PC) slab patterns.

The PL measurements were carried out using the same system in the above. However, for IR measurement, the detector used was the liquid N₂ cooled InGaAs detector, capable of measuring wavelength spectrum ranging from 1200 to 1700 nm. In this section, the Er:SRO/SiO₂ superlattice PC slab patterns were excited at wavelength of 488 nm. The excitation wavelength is weakly resonant to intra-4f energy levels of Erbium. However, the author has ensured that such resonance is not efficient by the absence of PL spectra of Er³⁺ ions peaked at 1.53 μm of the un-patterned Er:SiO₂ sample having the same Er concentration, treated with the same annealing procedure as those samples with 2D PC patterns, and measured using the same Micro-Raman PL system.

Figure 7.7 The (a) recorded and (b) normalized Er-related PL spectra for the un-patterned region and PC patterns Z5 ($a=1000$ nm, $\rho=0.34$), Z8 ($a=1500$ nm, $\rho=0.29$), and Z2 ($a=1500$ nm, $\rho=0.42$). The parameter a is lattice constant and ρ is the duty cycle (the ratio of air hole radius to the lattice constant)

From the discussion in section 7.3, it has been demonstrated that for the range of PC patterns in this work, the lattice constant plays much larger role than the duty cycle in promoting the enhancement of PL intensity. Figure 7.7(a) and 7.7(b) show the recorded and normalized PL intensity of un-patterned and PC patterns Z5 ($a=1000$ nm, $\rho=0.37$), Z8 ($a=1500$ nm, $\rho=0.29$), and Z2 ($a=1500$ nm, $\rho=0.42$). The excitation wavelength is strongly focussed on $3\mu\text{m}$ (3000 nm) diameter area on the surface of the structures. In Figure 7.6(b), the strongest PL enhancement by a factor of 3.5 is observed for sample Z2 which has the largest lattice constant of 1500 nm. The PL peak at $1.53\mu\text{m}$ corresponds to normalized frequency (a/λ) of ~ 1 , near Γ point of the TE-like leaky conduction. This means that the enhancement is closely related to the high Q-leaky modes. On the other hand, the pattern Z8, which has lattice constant of 1500 nm but smaller duty cycle of 0.29 , exhibits enhanced emission by a factor of 2.

Another interesting phenomenon is the effect of the wavelength-size cavities of the PC structure on the spontaneous emission rate of the Er ions. It is noted that the fabrication of penetrating

2D PC structures by etching process caused the partial removal of the active material. However, the spontaneous emission can also be compensated by Purcell spontaneous emission rate enhancement which occurs in the wavelength-size cavities of the PC structure due to the high quality factor [7-2] and small mode volume [7-11]. Furthermore, in the Er:SRO/SiO₂ superlattice PC pattern region, the change of the spontaneous emission rate (radiative lifetime) of Si nanostructures (700-800 nm) could also affect the energy transfer to Er ions. Also, the high pump power density could modify the Er spontaneous emission rate at 1.53 μm as well. Unfortunately, this effect is beyond the scope of this work because it requires a set up for lifetime measurements, which at the moment is not available.

7.5 Summary

In this chapter, the design of and experimental works on SRO/SiO₂ and Er:SRO/SiO₂ superlattice based triangular lattice air hole PC slab structures have been presented. The effects of two parameters of the 2D photonic crystal (PC) structure, namely: lattice constant (a) and duty cycles (ρ), on the enhancement of PL spectra of SRO/SiO₂ and Er:SRO/SiO₂ superlattice based 2D PC slabs have been discussed. The strongest enhancement was obtained for PC pattern with the largest lattice constant (a) in the series of patterns studied: $a=700$ nm for SRO/SiO₂ superlattice and $a=1500$ nm for Er:SRO/SiO₂ superlattice samples. The optimum duty cycle was found to be ~ 0.4 for both SRO/SiO₂ as well as Er:SRO/SiO₂ superlattice based 2D PC patterns. The possibility of studying the effect of wavelength size cavity of PC structure through Purcell Enhancement rate as well as the emission lifetime study can be interesting options for future work.

Chapter 8

Other Works: Development of Sputtered Silicon Oxynitride Material

8.1 Introduction

In this chapter, the author presents an additional work, which is on the development and characterizations of silicon oxynitride (SiON) films. One of the important characteristics of SiON is a wide range of the refractive index values, ranging from ~ 1.45 (close to refractive index of SiO_2) to ~ 2 (refractive index of Si_3N_4), which can be achieved by tailoring the atomic composition of its constituents: silicon (Si), oxygen (O) and nitrogen (N). Having the refractive index higher than that of silica (SiO_2), this material could potentially be used for various photonics applications.

One of the examples is the implementation of SiON as a host material for Si nanostructures which might be suitable for application of light emitting structure based on photonic crystal (PC) structures. With high index contrast, the photonic bandgap (PBG) effect might become more dominant as compared to lower refractive index material such as SiO_2 presented and discussed in Chapter 4 to 7. In term of the physics of light emission, the presence of oxygen (O) and nitrogen (N) bonds on the surface of Si nanostructures surely affect the mechanisms of light emission as well as the lifetime.

Another example is using the high refractive index and controllability of refractive index of SiON material for various passive and active optical waveguides especially at optical communication wavelength ($1.55 \mu\text{m}$) [8-1]-[8-5]. For many years, various passive and active SiON optical waveguides have been reported, reiterating its potential use for planar optical circuits on silicon [8-3]-[8-5]. However, in the past years, the development works on SiON material have been focused on the reduction of the propagation loss of SiON waveguides due to a fabrication related problem, namely N-H absorption, which becomes more prominent with increasing atomic concentration of nitrogen (N), i.e. higher refractive index [8-3], [8-5].

In view of these two potential applications, host for Si-nanostructures and optical waveguides, the author deposited SiON materials using RF sputter deposition methods and perform characterization works. In this chapter, the author limited the scope of the work to establish a good SiON material structure, which includes tailoring the refractive index of SiON thin film by tuning deposition process parameters, and reducing propagation loss of SiON slab waveguides.

8.2 Development of Silicon oxynitride thin films

To produce SiON films with controllable refractive index, ranging from ~ 1.45 (SiO_2) to ~ 2 (Si_3N_4), good deposition process parameters were established. In addition, SiON slab waveguides with low propagation loss were also developed and studied. In this section, preparation and characterization of SiON films will be presented.

8.2.1 Preparation of Silicon oxynitride thin films

To tailor the refractive index of SiON films with deposition parameters, three different sputter deposition processes, each using different sputtering targets, Silicon nitride (Si_3N_4), Silica (SiO_2), or Silicon (Si) were carried out. For all sputter deposition processes considered, the substrate temperature was kept constant at 100°C and the substrate was rotated at 20 rpm to ensure film thickness uniformity. The details of each deposition process and the resulting refractive index are presented in section 8.2.2 below.

8.2.2 Characterization of refractive index of SiON films

The refractive index is the most important parameter used to assess the feasibility of the sputtering technique to produce SiON thin films. To obtain the refractive index and thickness of each sample, the author used the spectroscopic ellipsometry (SE) technique, which has been discussed in Chapter 3 section 3.2.1.3. To confirm the fitting results, the thickness of the sample was independently measured using Surface profilometry technique discussed in Chapter 3 section 3.2.2.4.

8.2.2.1 Process I: sputtered Silicon Nitride (Si_3N_4) target

In the first process, Si_3N_4 target with 99.99 at.% purity was sputtered in the mixture of Argon (Ar) and Oxygen (O_2) gases. The Ar partial pressure was 10 mTorr, whereas the oxygen flow rate was varied from 0 to 5 sccm. For all samples, the RF power of Si_3N_4 target and the substrate temperature were kept constant at 300W and 100°C , respectively.

Figure 8.1 (a) Refractive indices at 632 nm and (b) deposition rates of as-deposited SiON films for different O₂ flow rates during deposition processes

Figures 8.1(a) and 8.1(b) show the refractive indices at 632 nm and the deposition rates of the as-deposited films for different O₂ flow rates during deposition process. In Figure 8.1(a), it can be seen that the refractive index of the film is very high (~ 2.4) when the flow rate of O₂ is zero. The refractive index decreases rapidly to ~ 1.6 and ~ 1.48 as the O₂ flow rate increases to 0.2 and 0.5 sccm. At O₂ flow rates larger than 1 sccm, the refractive index is almost constant at ~ 1.45 even when the flow rate of O₂ increases to 5 sccm. The above result shows that the refractive index of the as-deposited film is too sensitive to a small change of partial pressure of O₂.

At the flow rate of O₂ above 1 sccm, the as-deposited films have refractive indices very close to that of SiO₂, indicating that oxygen-containing plasma in this deposition process is much more reactive. This is probably due to the target surface poisoning by oxygen resulting in the formation of oxygen rich layer at the target surface. The sputtering rate by Ar gas cannot compete with the chemisorption of oxygen on the surface of Si₃N₄ target. A similar observation was also reported by Jones et al. [8-6] and Lounsbury et al. [8-7]. They have investigated the influence of oxygen partial pressure on the sputtering rate. In their work, a simple kinetic rate model was used to relate the flux of oxygen atoms to the surface with surface coverage (oxide layer) as well as sputtering rate and an agreement with experimental values was found [8-7]. The experimental values reported also indicated that surface target poisoning by the oxygen flux had reduced the sputtering rate by more than 50% even when the power was increased. From this particular experiment, it is difficult to achieve high

refractive index using Si_3N_4 target in oxygen containing plasma because of the high chemical reactivity of oxygen. In order to realize a high index film, nitrogen components from the target has to be incorporated into the film during the deposition.

8.2.2.2 Process II: sputtered Silica (SiO_2) target

Based on the results discussed above, the author used Silica (SiO_2) target with Ar and N_2 sputtering gas to tailor the refractive index of SiON . By incorporating a reactive nitrogen plasma, instead of the reactive oxygen plasma, the refractive index might be better tailored. For all deposition processes, the total gas pressure of Ar and N_2 was maintained at 8 mTorr, but the composition of partial pressures of Ar and N_2 were varied to obtain different nitrogen and oxygen content in the as-deposited films. For all samples, the RF power of SiO_2 target and substrate temperature were maintained at 250 Watts and 100°C , respectively.

Figure 8.2 (a) Refractive index (at 632 nm) as a function of the partial pressure of N_2 , and (b) the deposition rate as a function of the partial pressure of N_2 .

Figure 8.2 (a) and 8.2 (b) show, respectively, the refractive indices and the deposition rates for different partial pressures of N_2 gas. It is observed from Figure 8.2(a) that the refractive indices of the samples do not follow the expected monotonic increase with increasing N_2 partial pressure. With the absence of nitrogen in the plasma, the refractive index is expected to be around 1.46 close to that of SiO_2 films. Furthermore, with the increase of N_2 partial pressure, i.e. the increase of nitrogen content

in the plasma, the refractive index is expected to increase further. However, this is not observed in Figure 8.2(a). Instead, in the absence of N_2 flow rates, the refractive index is 1.652, deviating relatively far from that of SiO_2 films (1.46), indicating that the film is Si-rich oxide. Furthermore, the decrease of refractive index with the increase of N_2 partial pressure to 4 mTorr indicates that N atoms incorporated in the film and results in Si-N bonding replacing Si-Si bonds. In Figure 8.2(b), in the absence of nitrogen in the plasma, i.e. no N_2 partial pressure, the high deposition rates of 120 Å/minute results in non-stoichiometric films.

On the other hand, at partial pressure of N_2 of 4 mTorr and larger, the refractive index of deposited films increases as the partial pressure of N_2 increases. This indicates that the increase of refractive index is due to the increase of nitrogen incorporation into the thin film. The highest refractive index achievable using this process is 1.71. In Figure 8.2(b), it is shown that the deposition rate also decreases with increasing partial pressure of N_2 or decreasing Ar partial pressure. This can be explained by the fact that nitrogen is a less efficient sputtering ion than argon. For comparison, the mass of nitrogen ions ($M=14$ amu) is smaller than that of argon ($M=40$ amu). Therefore, the momentum and energy transfer of argon to silica target is larger than that of nitrogen.

8.2.2.3 Process III: sputtered Silicon target

The third process (process III) used was to deposit SiON films using Silicon (purity of 99.99%) target in Ar, N_2 and O_2 sputtering gas. The flow rates of both Ar and N_2 gases were kept constant at 28 sccm, whereas the flow rate of O_2 was varied within a small range from 0 sccm to 1 sccm. A fine resolution (full scale range of 5 sccm) mass flow controller (MFC) for O_2 gas is the important factor to produce well controlled inflow of oxygen into the deposition chamber. For all samples, the RF power of Si target and the substrate temperature were maintained at 250W and 100°C, respectively. Table 8.1 shows the RF powers applied on the target, the flow rate of each sputtering gas, and refractive indices of the as-deposited samples.

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Sample ID	Power (watts)	Flow rate of Ar/N ₂ /O ₂ (sccm)	As-deposited Refractive Index (at $\lambda=632$ nm)
S1	250	28/28/0	1.809
S2	250	28/28/0.04	1.764
S3	250	28/28/0.1	1.760
S4	250	28/28/0.12	1.730
S5	250	28/28/0.2	1.655
S6	250	28/28/0.25	1.632
S7	250	28/28/0.5	1.528
S8	250	28/28/0.75	1.494
S9	250	28/28/1.0	1.477

Table 8.1 The deposition parameters and refractive index of the as-deposited samples

Figure 8.3 (a) The refractive index of as-deposited samples determined by the spectroscopic ellipsometry technique as a function of oxygen (O₂) gas flow rate; (b) the deposition rate of as-deposited samples determined by surface profilometry technique as a function of O₂ gas flow rate.

Figure 8.3(a) shows the refractive index of as-deposited samples deposited using process III. A series of SiON samples with refractive index variation much wider than that of process I and II was obtained. As expected, as the O₂ flow rate increases, the refractive index decreases. However, at zero O₂ flow rate, the refractive index is below that of Si₃N₄, which could be due to the incorporation of Si-O bonds or incorporation of hydroxyl groups like O-H bonds from the remaining deep water vapour pressure in the chamber. It is also observed that a small increase of O₂ flow rate can decrease the

refractive index largely indicating that oxygen plasma is more reactive than nitrogen plasma. This can be related to the dynamics during incorporation of reactive oxygen and nitrogen into the surface layer of the Si target. The higher the flow rate (i.e. partial pressure) of the oxygen, the higher the rate of impingement of oxygen on the target surface, and therefore the larger the percentage of oxygen incorporated into the film.

In Figure 8.3(b), it is also observed that the deposition rates of the films slightly increase with the increase of oxygen partial pressure in the sputtering plasma. This can be explained by two possible reasons as follows. Firstly, O_2 has slightly higher mass than N_2 , hence the sputtering rate is slightly increased with the increase of oxygen plasma. Secondly a more oxygen-rich layer was formed with increasing oxygen plasma. Oxygen rich layer is more easily sputtered than nitride rich layer by Ar. This is supported by the deposition rates evidenced in the process I and II. In the absence of oxygen (process I) and nitrogen (process II), the deposition rate of sputtered SiO_2 is higher than Si_3N_4 , indicating that oxygen rich layer is more easily sputtered than nitride rich layer.

8.2.3 Infrared absorption of Silicon Oxynitride thin films

The study on three different sputter deposition processes of SiON has been discussed above. It is observed that the process III (the reactive sputtering of Si target using Ar, N, and O gasses) is a more feasible method to tailor the refractive index of SiON film. In this section, the author will discuss the absorption spectra of the SiON samples deposited using the process III.

Figure 8.4 Infrared (IR) O-Si-N absorption band (1400cm^{-1} - 600cm^{-1}) of the as-deposited samples for different O_2 gas flow rates, ranging from 0 to 1 sccm.

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Figure 8.4 shows O-Si-N absorption band (1400 cm^{-1} to 600 cm^{-1}) for different O_2 flow rates in process III. The absorption peak wavenumber shifts from 850 cm^{-1} (Si_3N_4 -like) to 1060 cm^{-1} (SiO_2 like) with the increase of O_2 flow rate from 0 to 1 sccm. This trend is better described in the inset of Figure 8.4. Furthermore, in Figure 8.3(a), it is shown that as the oxygen flow rate increases, the refractive index decreases. These results indicate that the variation of refractive index is related to the variation of nitrogen and oxygen bonded to Si in the as-deposited film matrix. From the same figure, it is also observed that the full-width half maximum (FWHM) of O-Si-N absorption band increases as the nitrogen concentration increases. This is because the presence of N atoms in the matrix creates more variation of network bonding arrangement in the SiON matrix [8-1].

The presence of O-H and N-H absorption bands is usually reported in SiON material systems. Being largely process-related, H could be bonded with Si, O, N atoms. The presence of hydrogen in the developed samples was mainly due to the presence of water vapour in the deposition chamber. The lowest base pressure, which usually consists of water vapour partial pressure, in the deposition process is around 3.5×10^{-7} Torr (assuming that 80-90% content of pressure below mTorr range is water vapor). A less hydrogen contaminated sputtered SiON film was usually deposited with base pressure at ultra-high vacuum at 10^{-9} Torr.

The first overtone of N-H and O-H stretching vibration is major source of absorption loss at optical communication window ($1.55\text{ }\mu\text{m}$) [8-1],[8-3],[8-8]. These two absorption bands (N-H and O-H) are usually reduced by annealing in inert gases such as N_2 , at high temperatures, ranging from 900°C to 1100°C . Figures 8.5(a) and 8.5(b) show the reduction of O-H and N-H absorption bands in sample S6 (refractive index of 1.632) and S1 (refractive index of 1.808) with the increase of annealing temperature. The absorption bands related to N-H and O-H stretching vibrations overlap with each other. However, it is known that the N-H stretching vibration is generally located at around 3360 cm^{-1} , while O-H stretching vibration represents a much broader absorption band, ranging from $3000\text{-}3600\text{ cm}^{-1}$ [8-1],[8-3],[8-8]. Therefore, it can also be observed that in sample S6 (see Figure 8.5(a)), the O-H absorption band is the more dominant absorption band, and in sample S1 (see Figure 8.5 (b)), the N-H absorption band is the dominant one. In Figure 8.5(a), after sample S6 is annealed at 1000°C or higher, the N-H and O-H stretching vibration bands is reduced to relatively small intensity. However, this does not apply generally to all samples. In Figure 8.5(b), N-H and O-H stretching vibrations still exist even after annealing at 1100°C . This is can be related to the increase of concentration of N-H bonds, which is quite resistant even under annealing at high temperatures [8-1].

(a)

(b)

Figure 8.5 The reduction of N-H and O-H absorption bands of (a) sample S6 (refractive index of 1.6323) (b) sample S1 (refractive index of 1.8088) after annealing treatment in N_2 at different temperatures.

Figure 8.6 O-Si-N IR absorption peak wavenumbers of sample S1 to S9 for different annealing conditions in the x-axis

Figure 8.6 shows the O-Si-N absorption peak wavenumbers of samples S1 to S9 after different annealing treatment at temperatures ranging from 900°C to 1100°C. All annealing treatment was performed in N_2 environment. It can be seen that for all samples, the O-Si-N absorption peak is consistently shifted to the higher wavenumber with the increase of annealing temperature and time. This could be explained by two mechanisms as follows: (i) the increase of film stress due to annealing at high temperature, which has been established to results in the shifting of O-Si-N absorption bands to higher wavenumbers [8-9], and (ii) the in-diffusion of oxygen into and out-diffusion of species such as NH_2 from the SiON film during long annealing process, which results in increase of Si-O bonding.

8.2.4 Slab Waveguide Loss Measurement

In order to investigate the effect of N-H and O-H on the propagation loss of SiON slab waveguide, SiON slab waveguides with guiding layer thicknesses around 1.5 μm were deposited. The thick films were deposited on the silicon (Si) substrate with top 10 μm thermally grown SiO_2 . The slab waveguide structure comprises of the SiO_2 layer as under cladding, air acts upper cladding, and thick SiON film as the core (guiding) layer. This structure is necessary so that the refractive index and the propagation loss can be measured using prism coupling technique. The working principle of this measurement technique has been explained in Chapter 3 section 3.4.

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Sample ID	Power (Watts)	Flow rate of Ar/N ₂ /O ₂ (sccm)	Thickness (μm)	As-deposited refractive index (at λ=1550 nm)
WG1	250	28/28/0	1.5	1.79
WG2	250	28/28/0.04	1.5	1.749
WG3	250	28/28/0.1	1.5	1.74
WG6	250	28/28/0.25	1.5	1.630

Table 8.2 The deposition parameters (sputter gas composition) and refractive index of the as-deposited samples

Table 8.2 shows the deposition parameters of the slab waveguides WG1, WG2, WG3, WG4, which were deposited to study the propagation loss in the SiON slab waveguides. The deposition process of the slab waveguide samples WG1, WG2, WG3, and WG4, corresponds, respectively, to sample S1, S2, S3, and S6. The as-deposited refractive indices of the samples were measured by prism coupling technique which has been described in Chapter 3 section 3.4. The SiON layer of each slab waveguide has thickness of 1.5 μm for all samples to accommodate at least two modes at 632 nm and one mode at 1550 nm.

Figure 8.7 Refractive index of slab SiON waveguide measured at wavelength of 1.55 μm as a function of annealing time at annealing temperature of 1100°C.

Figure 8.7 shows the refractive indices of as-deposited, annealed at 1100°C for 1 hour and 4 hours waveguide samples. It is clear that for all samples (WG1, WG2, WG3, and WG4), the refractive index decreases significantly when the sample is annealed at 1100°C, which were carried out to reduce absorption bands at 1.55 μm related to N-H and O-H stretching vibration. Such drop in

refractive index indicates that mechanisms other than film densification are present during annealing in N_2 . It is possibly due to the in-diffusion of oxygen as well as the release of nitride compounds, such as NH_3 , out of the SiON network.

Figure 8.8 The refractive index (left y-axis) and propagation loss at 1550 nm (right y-axis) of SiON slab waveguide sample WG4 as a function of annealing time at 1100°C in N_2 atmosphere

Figure 8.8 shows the propagation loss of the slab waveguide WG4, which was chosen because the sample has relatively high refractive index with propagation loss of 0.8, which is lower than 1 dB/cm, necessary for low-loss optical waveguiding application. The propagation loss (at 1550 nm) of each waveguides decreases significantly after annealing at 1100°C for 1 hour. This is attributed to the reduction of N-H, O-H as shown in Figure 8.5(a). Other defects could also be cured during post-annealing treatment, resulting in lower propagation loss in slab waveguides.

8.3 Summary

The discussion above focuses on the development of SiON thin film and slab waveguide structure with an objective to establish a good SiON thin film with, respectively, tailorable refractive index and low propagation loss. These objectives were successfully achieved using process III. By reactive sputtering of Si target with RF power of 250W in a mixture of Ar, O_2 , and N_2 sputtering gasses at substrate temperature of 100°C, silicon oxynitride (SiON) thin films with tailorable refractive index from ~1.46 to ~1.808 were demonstrated. Fourier Transform Infrared Spectroscopy

(FTIR) was used to analyze the hydrogen related bonds in the SiON samples for different annealing treatment. Subsequently, the propagation loss and refractive index of as-deposited and annealed (in N₂, at 1100°C for 1 hour and 4 hours) SiON slab waveguides were measured. It was found that the refractive index of all slab waveguide samples decreases with the increase of annealing time at 1100°C. This annealing treatment also reduces the propagation loss at 1.55 μm. For example, upon annealing at 1100°C for 4 hours, the refractive index of sample WG4 was reduced from 1.63 to 1.58, while the propagation loss at 1.55 μm was reduced from 1.45dB/cm to 0.8dB/cm, respectively. Such drop in refractive index indicates that mechanism other than film densification is present during annealing in N₂. Oxygen in-diffusion and release of nitride compounds, such as NH₂, out of the SiON network could be possible causes of the decrease of the refractive index upon annealing treatment.

Chapter 9

Conclusions and Recommendations

9.1 Conclusions

This chapter summarizes the results of this thesis and discusses some recommendations for future work. The results of this thesis would contribute to the concerted effort of realizing efficient light emission from Si nanostructures and also Si-nanostructures sensitized Erbium in Si compatible materials. The main conclusions drawn from the chapters of this thesis are presented below:

- In the literature review, the author presented a review on the emergence of Si nanostructures as a light emitter. To obtain controllable PL emission peak wavelength, the Si nanostructures size had to be controlled by process parameters. This narrowed down the choice of the material system into Si-rich oxide/SiO₂ (SRO/SiO₂) superlattice structure. Furthermore, the author also presented a review on the role of Si nanostructures as sensitizer for Er emission at 1.55 μm . One of the issues highlighted is the conflicting reported results on the dependence of Er emission on the size of Si nanostructures. To address this issue, a more appropriate approach using Er:Si-rich Oxide/SiO₂ (Er:SRO/SiO₂) superlattice structure was chosen. The choice of deposition process has also been reviewed in literature review. The co-sputter technique was chosen to deposit the SRO/SiO₂ and Er:SRO/SiO₂ superlattice structures due to the possibility of good controllability of Er doping into SRO layer as well as low cost preparation of the superlattice samples..
- In the literature review, it was observed that high thermal budget process, in the form of annealing at high temperature for prolonged time, was commonly used to promote the Si nanostructures. However, it is economically favourable to use low thermal budget processes, such as rapid thermal annealing (RTA) and excimer laser annealing (ELA) processes. The choice of low thermal budget process was supported by the previously reported works that effective clustering of Si occurs in the first few minutes of annealing.
- RF magnetron co-sputtering technique was used to deposit three SRO/SiO₂ superlattice samples with varying SRO layers thicknesses of 3 nm, 4 nm, and 5 nm. The SiO₂ layers for all samples were kept constant at 5 nm. The photoluminescence (PL) spectrum of each SRO/SiO₂ sample consists of three different PL bands, which are two oxygen deficiency

defect related PL emission bands at 400 nm and 515 nm and quantum confinement related PL emission band which corresponds to Si nanostructure sizes of 3.6, 4.6 and 6 nm.

- Hydrogen passivation in a forming gas (5% H_2 : N_2) at 500°C for 30 minutes of rapid annealed SRO/ SiO_2 superlattice samples enhanced the Si nanostructures related PL intensities by a factor of ~ 8 . It was also observed that PL peak intensity of passivated samples is higher by a factor of 1.5 to 1.7 than that of samples annealed in N_2 at 1000°C for 2 hours. The enhancement of PL peak intensity was related to hydrogen passivation of non-radiative recombination channels such as Pb-defect centres, i.e. Si dangling bonds on the surface of Si nanostructures, which are known to have large non-radiative recombination rate (exciton capture rate).
- Post-deposition control of Si nanostructure, i.e. PL peak wavelength, was demonstrated using two step RTA process, consisting of rapid annealing at in N_2 at 1100°C for 2 minutes and rapid oxidation in O_2 at 800°C for duration of 2 to 10 minutes of the superlattice samples. Upon oxidation for 2 and 10 minutes, Si nanocrystals with average size of 4 nm (as-deposited), reduced to 3.2 and 2 nm, respectively. The rate of change of PL peak wavelength (energy) is much faster than that at the latter stage of oxidation process. This is because for rapid annealed samples, the network was less densified due to the rapid heating and cooling of RTA process. Further enhancement of Si nanocrystals related PL intensity without reduction of nanocrystals size was achieved by annealing the oxidized samples in atmospheric ambient at 600°C, for 30 minutes. Upon annealing treatment in air ambient, Si nanocrystals related PL peak intensity increases by a factor of 2 and 7 for sample with the smallest and the largest nanocrystals size.
- The Er:SRO/ SiO_2 superlattice samples were prepared using RF magnetron co-sputtering technique. The samples were then rapid annealed in N_2 ambient for 2 minutes at temperatures ranging from 500°C to 1000°C. The Er related PL peak intensity (at 1.53 μm) increased with the increase of temperature and reaching optimum value at annealing at 850°C before decreasing at higher annealing temperatures. The PL peak intensity can be enhanced by passivation the samples, i.e. annealing in forming gas (5% H_2 : N_2) for 1 hour. However, after hydrogen passivation by annealing in FG (5% H_2 : N_2) for 1 hour, the Er related PL peak intensity for samples annealed at 500°C to 700°C (prior to passivation process) was effectively quenched. The absence of clustering in the TEM image of sample annealed at 700°C supported the argument that the Er ions were indirectly excited through defect-mediated energy transfer mechanism. On the other hand, the Er related PL peak intensity increases for samples annealed at temperatures ranging from 800°C to 1000°C (prior to passivation process). As the annealing temperature increases to 1000°C, the presence of Si

nanostructure becomes dominant. At optimum temperature of 1000°C, the TEM image showed that a mixture of Si nanocrystals and amorphous Si nanostructures was present. This is indicated that for passivated samples, Er emission is indirectly excited by the Si nanostructures-mediated energy transfer. The dependence of Er emission on Si nanostructure size has also been studied based on all passivated samples. The optimum Er PL peak intensity (at 1.53 μm) was observed for sample with Si nanostructure size of ~ 3.5 nm.

- The fabrication of two-dimensional (2D) triangular lattice of air hole photonic crystal (PC) slab structures based on SRO/SiO₂ and Er:SRO/SiO₂ superlattice samples was carried out. Prior to the fabrication process of 2D PC patterns, the PL emission of the two superlattice samples was optimized using the parameters established in the previous chapters, which are rapid annealing followed by passivation in forming gas (5% H₂:N₂). The 2D PC slab structure was designed to penetrate the active layer of the samples because of the capability of manipulating more light as compared to separated emitting layer and PC structure (extraction) region. Various 2D PC patterns with different geometrical parameters, such as lattice constant (a), air hole size (r), and duty cycle ($\rho=r/a$) were measured by micro-Raman photoluminescence (PL) spectroscopy. In general, the PL intensities of the regions with various PC patterns were enhanced as compared to un-patterned region. The strongest enhancement was obtained for PC pattern with the largest lattice constant (a) in the series of patterns studied: $a=700$ nm for SRO/SiO₂ superlattice and $a=1500$ nm for Er:SRO/SiO₂ superlattice samples. The optimum duty cycle was found to be ~ 0.4 for both SRO/SiO₂ as well as Er:SRO/SiO₂ superlattice based 2D PC patterns.
- In conclusion, the author has successfully demonstrated the use of low thermal budget and hydrogen passivation to realize the light emission from Si nanostructures and Si nanostructures-sensitized Er embedded in SiO₂, which was comparable or even higher than that of samples, treated using long conventional annealing method. Using SRO/SiO₂ superlattice approach, the size controllability of Si nanostructures as well as PL peak wavelength has been realized. The effect of passivation on the light emission of Si nanostructures as well as Er ion has also been studied. The passivation has been shown to enhance emission of Si nanostructures and Er. The 2D PC slab based on the developed superlattice has been fabricated and measured. A variation of enhancement of PL intensity which was largely dependent on the lattice constant (a) is observed.

9.2 Recommendations

Based on the work presented here, several recommendations for future works are outlined below:

- To establish the rapid thermal annealing (RTA) process for promoting Si nanostructures and Er emission in various embedding (host) systems, such as silicon oxynitride (SiON) and Silicon nitride (SiN), which are more attractive for electrically injected light emitting structures
- With established fabrication process of two-dimensional photonic crystal (PC) slab based on active materials, the progress towards electrically injected light emitting 2D PC slab structure capable of enhancing light output can be realized.
- To study the lifetime of Si nanostructures and Er emission to establish better understanding of the energy transfer mechanisms and other competing radiative and non-radiative recombination channels in the Si nanostructures and Si nanostructures sensitized Er in SiO₂ system. It is also understood that the presence of PC structure results in modification of spontaneous emission of active materials, including that of Si nanostructures and Er ions. A suitable set up to measure emission lifetime and intensity is important to obtain several parameters which will be useful for optimizing the light emitting devices.
- The possibility of studying the effect of wavelength size cavity of PC structure through Purcell Enhancement rate as well as the emission lifetime study can be interesting options for future work.

Author's Publications

[Paper-I] Samson T. H. Silalahi, H.Y. Yang, K. Pita, and Yu Mingbin, "Rapid Thermal Annealing of Sputtered Silicon-Rich Oxide/SiO₂ Superlattice Structure", *Electrochemical and Solid-State Letters*, 12 (2009) K29-K32

[Paper-II] Samson T. H. Silalahi, H.Y. Yang, Q.V. Vu, K. Pita, Yu Mingbin, "Size control of Sputtered Silicon-rich Oxide Superlattice Structure by Two-step Rapid Thermal Annealing", (accepted for publication in *Applied Physics A: Material Science & Processing*)

[Paper-III] Samson T. H. Silalahi, Rui Chen, Q.V. Vu, K. Pita, H.D. Sun, and M.B. Yu, "The Effects of Rapid Annealing and Passivation of co-sputtered Er:Si-rich Oxide/SiO₂ Superlattice Structures" (submitted to and under review in *Applied Physics Letters*)

[Paper-IV] Samson T. H. Silalahi, Yu Mingbin, and K. Pita "Un-doped and Erbium-doped Si-rich Oxide Superlattice based Photonic Crystal Slab Structures" (prepared for submission)

Bibliography

- [1-1] G. E. Moore, "Cramming more components onto integrated circuits", *Electronics*, 38 (1965)
- [1-2] Semiconductor Industry Association, *International Technology Roadmap for Semiconductors: 1999 Edition*, Austin, Texas: International SEMATECH (1999) 163-186
- [1-3] P. C. Andriacos, "Copper on-chip interconnections, a breakthrough in electrodeposition to make better chips", *The Electrochemical Society Interface*, (1999) 32-37
- [1-4] H. Sanchez, "Design implications of low-k", *Proceedings of the IEEE 2003 International Interconnect Technology Conference*, (2003) 3-5
- [1-5] A. F. J. Levi, "Optical Interconnects in Systems", *Proceedings of the IEEE*, 88 (2000) 750-757
- [1-6] D.A.B. Miller, "Rationale and Challenges for Optical Interconnects to Electronic Chips", *Proceedings of the IEEE*, 88 (2000) 728-749
- [1-7] Bahram Jalali, and Sasan Fathpour, "Silicon Photonics", *Journal of Lightwave Technology*, 24 (2006) 4600-4615
- [1-8] L. Pavesi and Guillot, *"Optical Interconnects: The Silicon Approach"*, Berlin, New York: Springer-Verlag (2006)
- [1-9] B. Jalali, V.Raghunathan, R. Shori, S. Fathpour, D. Dimitropoulos, and O. Stafsudd, "Prospects for Silicon Mid-IR Raman Lasers", *IEEE Journal of Selected Topics on Quantum Electronics*, 12 (2006) 1618-1627
- [1-10] R. A. Soref, J. Schmidtchen, and K. Petermann, "Large single-mode rib waveguides in GeSi and Si-on-SiO₂", *IEEE Journal of Quantum Electronics*, 27 (1991) 1971-1974
- [1-11] Y. A. Vlasov and S. McNab, "Losses in single-mode silicon-on-insulator strip waveguides and bends", *Optics Express*, 12 (2004) 1622-1631
- [1-12] H. K. Tsang, C. S. Wong, and T. K. Liang, I. E. Day, S. W. Roberts, A. Harpin, J. Drake, and M. Asghari, "Optical dispersion, two-photon absorption and self-phase modulation in silicon waveguides at 1.5 μm wavelength", *Applied Physics Letters*, 80 (2002) 416-418
- [1-13] Vilson R. Almeida, Carlos A. Barrios, Roberto R. Panepucci & Michal Lipson, "All-optical control of light on a silicon chip", *Nature*, 431 (2004) 1081-1084
- [1-14] G. T. Reed, and C. E. Png, "Silicon optical modulators", *Materials Today*, 8 (2005) 40-50
- [1-15] L. Liao, D. Samara-Rubio, M. Morse, A. Liu, D. Hodge, D. Rubin, U. Keil, and T. Franck, "High speed silicon Mach-Zehnder modulator", *Optics Express*, 13 (2005) 3129-3135
- [1-16] D. J. Lockwood, R. Willardson, Eicke Weber, "Light emission in silicon: from physics to devices", *Semiconductor and Semimetals*, 49 (1997)
- [1-17] G. Roelkens, J. Brouckaert, J. Van Campenhout, D. Van Thourhout, R. Baets, "Heterogeneous Integration of III-V Active Devices on a Silicon-on-Insulator Photonic Platform", *4th IEEE International Conference on Group IV Photonics*, (2007) 1-3
- [1-18] J. Van Campenhout, P. Rojo Romeo, P. Regreny, C. Seassal, D. Van Thourhout, S. Verstuyft, L. Di Cioccio, J.-M. Fedeli, C. Lagahe, and R. Baets, "Electrically pumped InP-based microdisk lasers integrated with a nanophotonic SOI waveguide circuit", *Optics Express*, 15 (2007) 6744-6749

-
- [1-19] G. Roelkens, D. Van Thourhout, R. Baets, "Heterogeneous Integration of III-V Membrane Devices and Ultracompact SOI Waveguides, *IEEE LEOS Summer Topicals*, (2004) 23-24
- [1-20] P. Bettotti, M. Cazzanelli, L. Dal Negro, B. Danese, Z. Gaburro, C. J. Oton, G. Vijaya Prakash, and L. Pavesi, "Silicon nanostructures for photonics", *Journal of Physics: Condensed Matter*, 14 (2002) 8253-8281
- [1-21] D. Kovalev, H. Heckler, G. Polisski, and F. Koch, "Optical Properties of Si Nanocrystals", *Physica Status Solidi B*, 215 (1999) 871-932
- [1-22] Johannes Heitmann, Frank Muller, Lixin Yi, and Margit Zacharias, Dmitri Kovalev, and Frank Eichhorn, "Excitons in Si nanocrystals: Confinement and migration effects", *Physical Review B*, 69 (2004) 195309 (1-7)
- [1-23] Ching-Song Yang, Chrong-Jung Lin, Ping-Yu Kuei, Sheng-Fu Horng, Charles Ching-Hsiang Hsu, and Ming-Chi Liaw, "Quantum size effects on photoluminescence from Si nanocrystals in PECVD silicon-rich-oxide", *Applied Surface Science*, 113-114 (1997) 116-120
- [1-26] G. Allan, C. Delerue, and M. Lannoo, "Electronic Structure of Amorphous Silicon Nanoclusters", *Physical Review Letters*, 78 (1997) 3161-3164
- [1-27] 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*, 82 (1999) 197-200.
- [1-28] A. Podhorodecki, J. Misiewicz, F. Gourbilleau, and R. Rizk, "Absorption Mechanisms of Silicon Nanocrystals in Cosputtered Silicon-Rich-Silicon Oxide Films", *Electrochemical and Solid State Letters*, 11 (2008) K31-K33
- [1-29] K. Watanabe, M. Fujii, and S. Hayashi, "Resonant excitation of Er^{3+} by the energy transfer from Si nanocrystals", *Journal of Applied Physics*, 90 (2001) 4761-4767
- [1-30] M. Luppi, and S. Ossicini, "Ab initio study on oxidized silicon clusters and silicon nanocrystals embedded in SiO_2 : Beyond the quantum confinement effect *Physical Review B - Condensed Matter and Materials Physics*, 71 (2005) 1-15
- [1-31] M. L. Bongersma, A. Polman, K.S. Min, E. Boer, T. Tambo, and H. A. Atwater, "Tuning the emission wavelength of Si nanocrystals in SiO_2 by oxidation", *Applied Physics Letters*, 72 (1998) 2577-2579
- [1-32] Fabio Iacona, Giorgia Franzo, and Corrado Spinella "Correlation between luminescence and structural properties of Si nanocrystals", *Journal of Applied Physics*, 87 (2000) 1295-1303
- [1-33] G. Franzò, M. Miritello, S. Boninelli, R. Lo Savio, M. G. Grimaldi, F. Priolo, F. Iacona, G. Nicotra, C. Spinella, and S. Coffa, "Microstructural evolution of SiO_x films and its effect on the luminescence of Si nanoclusters", *Journal of Applied Physics*, 104 (2008) 094306 (1-5)
- [1-34] A. Morales, J. Barreto, C. Dominguez, M. Riera, M. Aceves, and J. Carrillo, "Comparative study between silicon-rich oxide films obtained by LPCVD and PECVD", *Physica E, Low-dimensional Systems and Nanostructures*, 38 (2007) 54-58
- [1-35] V. Kapaklis, C. Politis, P. Pouloupoulos, P. Schweiss, "Photoluminescent Si nanoparticles embedded in silicon oxide matrix", *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, 124-125 (2005) 475-478
- [1-36] M. Zacharias, J. Heitmann, R. Scholz, and U. Kahler, M. Schmidt, and J. Blasing, "Size-controlled highly luminescent silicon nanocrystals: A SiO/SiO_2 superlattice approach", *Applied Physics Letters*, 80 (2002) 661-663
- [1-37] S. Dongwook, "Photoluminescence of erbium-doped silica-based waveguide film via flame hydrolysis deposition and aerosol doping", *Journal of Ceramic Processing Research* 7 (2006) 379-383
-

-
- [1-38] K. Hattori, T. Kitagawa, M. Oguma, Y. Ohmori, and M. Horiguchi, "Erbium-doped Silica-based Waveguide Amplifier Integrated with a 980/1530nm WDM Coupler", *Electronics Letters*, 30 11 (1994) 856-857
- [1-39] T. Kitagawa, K. Hattori, K. Shuto, M. Yasu, M. Kobayashi, and M. Horiguchi, "Amplification in erbium-doped silica based planar lightwave circuits", *Electronics Letters*, 28 (1992) 1818-1819
- [1-40] K. Hattori, T. Kitagawa, M. Oguma, M. Horiguchi, M. Wada, and J. Temmyo, "Erbium-doped silica-based planar waveguide amplifier pumped by 0.98 μm laser diodes", *Electronics Letters*, 29 (1993) 357-359
- [1-41] L. Zampedri, M. Ferrari, C. Armellini, F. Visintainer, C. Tosello, S. Ronchin, R. Rolli, M. Montagna, A. Chiasera, S. Pelli, G.C. Righini, A. Monteil, C. Duverger and R.R. Gonçalves, "Erbium activated silica-titania planar waveguides", *Journal of Sol-Gel Science and Technology*, 26 (2003) 1033-1036
- [1-42] Y.C. Yan, A.J. Faber, H. de Waal, A. Polman, and P.G. Kik, "Erbium-doped phosphate glass waveguide on silicon with 4.1 dB/cm gain at 1.535 μm ", *Applied Physics Letters*, 71 (1997) 2922-2924
- [1-43] R. Francini, F. Giovenale, U.M. Grassano, P. Laporta, and S. Taccheo, "Spectroscopy of Er and Er-Yb-doped phosphate glasses", *Optical Materials*, 13 (2000) 417-425
- [1-44] C. Urlacher, C. Marco de Lucas, E. Bernstein, B. Jacquier, and J. Mugnier, "Study of erbium doped ZrO_2 waveguides elaborated by a sol-gel process", *Optical Materials*, 12 (1999) 19-25
- [1-45] Ross Schermer, Carol Ford, Randy Ramberg, and Anand Gopinath, "Optical amplification at 1534 nm in Er-doped Zirconia Waveguides", *IEEE Journal of Quantum Electronics*, 39 1 (2003) 154-159
- [1-46] G. N. van den Hoven, A. Polman, C. van Dam, J. W. M. van Uffelen, and M. K. Smith, "Net optical gain at 1.53 μm in Er-doped Al_2O_3 waveguides on silicon," *Applied Physics Letters*, 68 (1996) 1886-1888
- [1-47] G. N. van den Hoven, E. Snoeks, A. Polman, C. van Dam, J.W. M. van Uffelen, and M. K. Smit, "Upconversion in Er-implanted Al_2O_3 waveguides," *J. Appl. Phys.*, 79, 1258-1266 (1996)
- [1-48] A. Polman, "Erbium implanted thin film photonic materials", *Journal of Applied Physics*, 82 (1997) 1-39
- [1-49] P. G. Kik, M. L. Brongersma, and A. Polman, "Strong exciton-erbium coupling in Si nanocrystal-doped SiO_2 ", *Applied Physics Letters*, 76 (2000) 2325-2327
- [1-50] M. Fujii, K. Imakita, K. Watanabe, and S. Hayashi, "Coexistence of two different energy transfer processes in SiO_2 films containing Si nanocrystals and Er", *Journal of Applied Physics*, 95 (2004) 272-280
- [1-51] Oleksandr Savchyn and Pieter G. Kik, Ravi M. Todi and Kevin R. Coffey, "Effect of hydrogen passivation on luminescence-center-mediated Er excitation in Si-rich SiO_2 with and without Si nanocrystals", *Physical Review B*, 77 (2008) 205438 (1-11)
- [1-52] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, and K. Yamamoto, "1.54- μm photoluminescence of Er^{3+} doped into SiO_2 films containing Si nanocrystals: evidence for energy transfer from Si nanocrystals to Er^{3+} ", *Applied Physics Letters*, 71 (1997) 1198-1200
- [1-53] C. L. Heng, O. H. Y. Zalloum, J. Wojcik, T. Roschuk, and P. Mascher, "On the effects of double-step anneal treatments on light emission from Er-doped Si-rich silicon oxide", *Journal of Applied Physics*, 103 (2008) 024309 (1-9)
-

-
- [1-54] Tetsuya Makimura, Hiroshi Uematsu, Yuuki Okada and Kouichi Murakami, "1.5 μm light emission of Er^{3+} ions doped in SiO_2 films including Si nanocrystallites and in SiO_x films", *Journal of Physics: Conference Series*, 59 (2007) 466–469
- [1-55] B. Salem, P. Noe, F. Mazen, V. Calvo, E. Hadji, "Photoluminescence from Er-doped silicon rich oxide thin films", *Journal of Luminescence*, 121 (2006) 242–244
- [1-56] F. Priolo, G. Franzo', D. Pacifici, V. Vinciguerra, F. Iacona, and A. Irrera, "Role of the energy transfer in the optical properties of undoped and Er-doped interacting Si nanocrystals", *Journal of Applied Physics*, 89 (2001) 264
- [1-57] J. Shakya, K. H. Kim, J. Y. Lin, and H. X. Jiang, "Enhanced light extraction in III-nitride ultraviolet photonic crystal light-emitting diodes", *Applied Physics Letters*, 85 (2004) 142–144
- [1-58] Shanhui Fan, Pierre R. Villeneuve, and J. D. Joannopoulos, and E. F. Schubert, "High Extraction Efficiency of Spontaneous Emission from Slabs of Photonic Crystals", *Physical Review Letters*, 78 (1997) 3294–3297
- [1-59] M. Boroditsky, T. F. Krauss, R. Coccioli, R. Vrijen, R. Bhat, and E. Yablonovitch, "Light extraction from optically pumped light-emitting diode by thin-slab photonic crystals", *Applied Physics Letters*, 75 (1999) 1036–1038
- [1-60] A. A. Erchak, D. J. Ripin, S. Fan, P. Rakich, J. D. Joannopoulos, E. P. Ippen, G. S. Petrich, and L. A. Kolodziejski, "Enhanced coupling to vertical radiation using a two-dimensional photonic crystal in a semiconductor light-emitting diode", *Applied Physics Letters*, 78 (2001) 563
- [2-1] Bahram Jalali, and Sasan Fathpour, "Silicon Photonics", *Journal of Lightwave Technology*, 24 (2006) 4600–4615
- [2-2] D. A. B. Miller, "Optical interconnects to silicon", *IEEE Journal of Selected Topics on Quantum Electronics*, 6 (2000) 1312–1317
- [2-3] "Silicon photonics vision", Intel (2006)
- [2-4] L. Pavesi and Guillot, "*Optical Interconnects: The Silicon Approach*", Berlin, New York: Springer-Verlag (2006)
- [2-5] M. Haurylau, G. Chen, H. Chen, J. Zhang, N.A. Nelson, D. H. Albonesi, E. G. Friedman, and P. M. Fauchet, "On-chip optical interconnect roadmap: challenges and critical directions", *IEEE Journal of Selected Topics in Quantum Electronics, Special Issue on Silicon Photonics*, 12 (2006) 1699–1705
- [2-6] C. Gunn, "CMOS photonics for high-speed interconnects," *IEEE Micro*, 26 (2006) 58–66
- [2-7] G. T. Reed, and C. E. Png, "Silicon optical modulators," *Materials Today*, 8 (2005) 40–50
- [2-8] L. Liao, D. Samara-Rubio, M. Morse, A. Liu, D. Hodge, D. Rubin, U. Keil, and T. Franck, "High speed silicon Mach–Zehnder modulator," *Optics Express*, 13 (2005) 3129–3135
- [2-9] R. A. Soref, J. Schmidtchen, and K. Petermann, "Large single-mode rib waveguides in GeSi and Si-on- SiO_2 ", *IEEE Journal of Quantum Electronics*, 27 (1991) 1971–1974
- [2-10] J. Takahashi, T. Tsuchizawa, T. Watanabe, and S. Itabashi, "Oxidation induced improvement in the sidewall morphology and cross-sectional profile of silicon wire waveguides," *Journal of Vacuum Science Technology B*, 22 (2004) 2522–2525
- [2-11] Y. A. Vlasov and S. McNab, "Losses in single-mode silicon-on-insulator strip waveguides and bends," *Optics Express*, 12 (2004) 1622–1631
-

-
-
- [2-12] M. Loncar, D. Nedeljkovic, T. Doll, J. Vuckovic, A. Scherer, and T. P. Pearsall, "Waveguiding in planar photonic crystals", *Applied Physics Letters*, 77 (2000) 1937-1939
 - [2-13] S. J. McNab, N. Moll, and Y. A. Vlasov, "Ultra-low loss photonic integrated circuit with membrane-type photonic crystal waveguides", *Optics Express*, 11 (2003) 2927 (2003)
 - [2-14] Thomas Kubarsepp, Atte Haapalinna, Petri Karha, and Erkki Ikonen, "Nonlinearity measurements of silicon photodetectors", *Applied Optics*, 37 (1998) 2716-2722
 - [2-15] B. Jalali, V. Raghunathan, R. Shori, S. Fathpour, D. Dimitropoulos, and O. Stafsudd, "Prospects for Silicon Mid-IR Raman Lasers", *IEEE Journal of Selected Topics on Quantum Electronics*, 12 (2006) 1618-1627
 - [2-16] Jaime Cardenas, Carl B. Poitras, Jacob T. Robinson, Kyle Preston, Long Chen, and Michal Lipson, "Low loss etchless silicon photonic waveguides", *Optics Express*, 17 (2009) 4752-4757
 - [2-17] D. Wood, "Optoelectronic Semiconductor Devices", Trowbridge, U.K.: Prentice-Hall (1994)
 - [2-18] J. Michel, J. F. Liu, W. Giziewicz, D. Pan, K. Wada, D. D. Cannon, S. Jongthammanurak, D. T. Danielson, L. C. Kimerling, J. Chen, F. O. Ilday, F. X. Kartner, and J. Yasaitis, "High performance Ge p-i-n photodetectors on Si," *IEEE International Conference on Group IV Photonics*, (2005) 177-179
 - [2-19] S. M. Csutak, J. D. Schaub, S. Wang, J. Mogab, and J. C. Campbell, "Integrated silicon optical receiver with avalanche photodiode", *IEEE Proceedings-Optoelectronics*, 150 (2003) 235-237
 - [2-20] G. Dehlinger, J. D. Schaub, S. J. Koester, Q. C. Ouyang, J. O. Chu, and A. Grill, "High-speed germanium-on-insulator photodetectors", *Lasers and Electro-Optics Society, The 18th Annual Meeting of the IEEE*, (2005) 321-322
 - [2-21] M. Jutzi, M. Berroth, G. Wohl, M. Oehme, and E. Kasper, "Ge-on-Si vertical incidence photodiodes with 39-GHz bandwidth", *IEEE Photonics Technology Letters*, 17 (2005) 1510-1512
 - [2-22] D. J. Lockwood, R. Willardson, Eicke Weber, "Light emission in silicon: from physics to devices", *Semiconductor and Semimetals*, 49 (1997)
 - [2-23] P. A. Badoz, L. Garchery, and A. Halimaoui, "Physical and characterization of silicon and porous silicon based electroluminescence diodes", *Proceedings of the 7th International Symposium on Silicon Materials Science and Technology*, 94-10 (1994) 569-574
 - [2-24] U. Gosele, "Nanocrystals: shedding new light on silicon", *Nature Nanotechnology*, 3 (2008) 134-135
 - [2-25] L. Dal Negro, J. H. Yi, H. Koklu, J. Michel, L. C. Kimerling, "Light emission from silicon-based nano-materials", *Conference Proceedings - Lasers and Electro-Optics Society Annual Meeting-LEOS*, 4054298 (2007) 544
 - [2-26] T. J. Clement, R. G. DeCorby, N. Ponnampalam, T. W. Allen, A. Hryciw, A. Meldrum, "Nanocluster sensitized erbium-doped silicon monoxide waveguides", *Optics Express* 14 (2006) 12151-12162
 - [2-27] S. Moon, B. H. Kim, P. R. Watekar, W. -T. Han, "Fabrication and photoluminescence characteristics of Er³⁺-doped optical fiber sensitized by Si particles", *Journal of Non-Crystalline Solids*, 353 (2007) 2949-2953
-
-

-
- [2-28] V. Lehmann, and U. Gosele, "Porous silicon formation: A quantum wire effect", *Applied Physics Letters*, 58 (1991) 856-858
- [2-29] P. Bettotti, M. Cazzanelli, L. Dal Negro, B. Danese, Z. Gaburro, C. J. Oton, G. Vijaya Prakash, and L. Pavesi, "Silicon nanostructures for photonics", *Journal of Physics: Condensed Matter*, 14 (2002) 8253-8281
- [2-30] D. Kovalev, H. Heckler, G. Polisski, and F. Koch, "Optical Properties of Si Nanocrystals", *Physica Status Solidi B*, 215 (1999) 871-932
- [2-31] X. X. Wang, J. G. Zhang, L. Ding, B. W. Cheng, W. K. Ge, J. Z. Yu, and Q. M. Wang "Origin and evolution of photoluminescence from Si nanocrystals embedded in a SiO₂ matrix", *Physical Review B*, 72 (2005) 195313 (1-6)
- [2-32] S. Zhang, W. Zhang, J. Yuan, "The preparation of photoluminescent Si nanocrystal-SiO_x films by reactive evaporation", *Thin Solid Films*, 326 (1998) 92-98
- [2-33] J. B. Khurgin, E. W. Forsythe, S. I. Kim, B. S. Sywe, B. A. Khan, and G.S. Tompa, "Influence of the dispersion of the size of the Si nanocrystals on their emission spectra", *Materials Research Society Symposium – Proceedings*, 358 (1995) 193-197
- [2-34] M. L. Bongersma, K. S. Min, E. Boer, T. Tambo, A. Polman, H. A. Atwater, "Tailoring the optical properties of Si nanocrystals in SiO₂: materials issues and nanocrystal laser perspectives", *Materials Research Society Symposium - Proceedings* 486 (1998) 213-218
- [2-35] J. N. Milgram, J. Wojcik, P. Mascher, A. P. Knights, "Optically pumped Si nanocrystal emitter integrated with low loss silicon nitride waveguides", *Optics Express* 15 (2007) 14679-14688
- [2-36] A. G. Cullis, L.T. Canham, and P.D. J. Calcott, "The structural and luminescence properties of porous silicon", *Journal of Applied Physics*, 82 (1997) 909-965
- [2-37] O. Bisi, S. Ossicini and L. Pavesi, "Porous silicon: a quantum sponge structure for silicon based optoelectronics", *Surface Science Reports*, 38 (2000) 1-126
- [2-38] R. L. Smith, and S. D. Collins, "Porous silicon formation mechanisms", *Journal of Applied Physics*, 71 (1992) R1-R22
- [2-39] 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*, 82 (1999) 197-200.
- [2-40] A. Foucaran, F. Pascal-Delannoy, A. Giani, A. Sackda, P. Combette and A. Boyer, "Porous silicon layers used for gas sensor applications", *Thin Solid Films*, 297 (1997) 317-320
- [2-41] Lenward Seals, James L. Gole, Laam Angela Tse and Peter J. Hesketh, "Rapid, reversible, sensitive porous silicon gas sensor", *Journal of Applied Physics*, 91 (2002) 2519-2523
- [2-42] T. K. Gupta, and J. H. Jean, "Principles of the development of a silica dielectric for microelectronics packaging", *Journal of Materials Research*, 11 (1996) 243-263
- [2-43] N. Novkovsi, and E. Atanassova, "Approaching the limit of the SiO₂ possibilities for application in nanoscale microelectronics", *Journal of optoelectronics and advanced materials*, 8 (2006) 1238-1242
- [2-44] S. Huang, H. Xiao, S. Shou, "Annealing temperature dependence of Raman scattering in Si/SiO₂ superlattice prepared by magnetron sputtering", *Applied Surface Science*, 255 (2009) 4547-4550
- [2-45] S. Charvet, R. Madelon, F. Gourbilleau, and R. Rizk, "Spectroscopic ellipsometry analyses of sputtered Si/SiO₂ nanostructures", *Journal of Applied Physics*, 85 (1999) 4032-4039
-

-
- [2-46] P. G. Kik, A. Polman, "Exciton-erbium energy transfer in Si nanocrystal-doped SiO₂", *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, 81 (2001) 3-8
- [2-47] K. Seino, F. Bechstedt, P. Kroll, "Influence of SiO₂ matrix on electronic and optical properties of Si nanocrystals", *Nanotechnology*, 20 (2009) 135702
- [2-48] C. Bulutay, "Electronic structure and optical properties of silicon nanocrystals along their aggregation stages", *Physica E: Low-Dimensional Systems and Nanostructures*, 38 (2007) 112-117
- [2-49] M. Porti, M. Avidano, M. Nafria, X. Aymerich, J. Carreras, B. Garrido, "Charge storage in Si nanocrystals embedded in SiO₂ with enhanced C-AFM", *Proceedings of SPIE - The International Society for Optical Engineering*, 5838 (2005) 43-51
- [2-50] Johannes Heitmann, Frank Muller, Lixin Yi, and Margit Zacharias, Dmitri Kovalev, and Frank Eichhorn, "Excitons in Si nanocrystals: Confinement and migration effects", *Physical Review B*, 69 (2004) 195309 (1-7)
- [2-51] K. C. Sheer, R.A. Rao, R. Muralidhar, S. Bagchi, J. Conner, L. Lozano, C. Perez, M. Sadd, and B.E. White Jr, "Thermal oxidation of silicon nanocrystals in O₂ and NO ambient", *Journal of Applied Physics*, 93(2003) 5637-5642
- [2-52] G. Allan, C. Delerue, and M. Lannoo, "Electronic Structure of Amorphous Silicon Nanoclusters", *Physical Review Letters*, 78 (1997) 3161-3164
- [2-53] M. Zacharias, J. Heitmann, R. Scholz, U. Kahler, M. Schmidt, and J. Blasing, "Size-controlled highly luminescent silicon nanocrystals: A SiO/SiO₂ superlattice approach", *Applied Physics Letters*, 80 (2002) 661-663
- [2-54] L. X. Yi, J. Heitmann, R. Scholz and M. Zacharias, "Phase separation of thin SiO layers in amorphous SiO/SiO₂ superlattices during annealing", *Journal of Physics: Condensed Matter*, 15 (2003) S2887-S2895
- [2-55] Leonid Khriachtchev, Olli Kilpela, Suvi Karirinne, Jaako Keranen, and Toivo Lepisto, "Substrate-dependent crystallization and enhancement of visible photoluminescence in thermal annealing of Si/SiO₂ superlattices", *Applied Physics Letters*, 78 (2001) 323-325
- [2-56] W. J. Miniscalco, "Erbium-doped glasses for fiber amplifiers at 1500 nm", *J. Lightwave Technol.*, 9 (1991) 234-250
- [2-57] E. Desurvire, "Erbium-Doped Fiber Amplifiers: Principles and Applications" (Wiley, New York, 1994).
- [2-58] P.G. Kik, and A. Polman, "Erbium doped optical waveguide amplifiers on silicon", *MRS Bulletin*, 23 (1998) 48
- [2-59] S. Huffner, "Optical Spectra of Transparent Rare-Earth Compounds" Academic, New York, 1978)
- [2-60] A. Polman, "Erbium implanted thin film photonic materials", *Journal of Applied Physics*, 82 (1997) 1-39
- [2-61] R. Francini, F. Giovenale, U.M. Grassano, P. Laporta, and S. Taccheo, "Spectroscopy of Er and Er-Yb-doped phosphate glasses", *Optical Materials*, 13 (2000) 417-425
- [2-62] N.V. Gaponenko, V. Mudryi, E. A. Stepanova, A. I. Ratko, O.V. Sergeev, and V.E. Borisenko, "Photoluminescence of sol-gel-prepared erbium-doped alumina films", *Inorganic Materials*, 34 (1998) 795-799
- [2-63] K. Hattori, T. Kitagawa, M. Oguma, Y. Ohmori, and M. Horiguchi, "Erbium-doped Silica-based Waveguide Amplifier Integrated with a 980/1530nm WDM Coupler", *Electronics Letters*, 30 11 (1994) 856-857
-

-
- [2-64] T. Kitagawa, K. Hattori, K. Shuto, M. Yasu, M. Kobayashi, and M. Horiguchi, "Amplification in erbium-doped silica based planar lightwave circuits", *Electronics Letters*, 28 (1992) 1818–1819
- [2-65] K. Hattori, T. Kitagawa, M. Oguma, M. Horiguchi, M. Wada, and J. Temmyo, "Erbium-doped silica-based planar waveguide amplifier pumped by 0.98 μm laser diodes", *Electronics Letters*, 29 (1993) 357–359
- [2-66] L. Zampedri, M. Ferrari, C. Armellini, F. Visintainer, C. Tosello, S. Ronchin, R. Rolli, M. Montagna, A. Chiasera, S. Pelli, G.C. Righini, A. Monteil, C. Duverger and R.R. Gonçalves, "Erbium activated silica-titania planar waveguides", *Journal of Sol-Gel Science and Technology*, 26 (2003) 1033–1036
- [2-67] Y.C. Yan, A.J. Faber, H. de Waal, A. Polman, and P.G. Kik, "Erbium-doped phosphate glass waveguide on silicon with 4.1 dB/cm gain at 1.535 μm ", *Applied Physics Letters*, 71 (1997) 2922–2924
- [2-68] M. B. Korzenski, Ph. Lecoœur, B. Mercey, P. Camy and J. L. Doualan, "Low propagation losses of an Er:Y₂O₃ planar waveguide grown by alternate-target pulsed laser deposition", *Applied Physics Letters*, 78 (2001) 1210–1212
- [2-69] H. Guo, W. Zhang, L. Lou, A. Brioude, and J. Mugnier, "Structure and optical properties of rare earth doped Y₂O₃ waveguide films derived by sol–gel process", *Thin Solid Films*, 458 (2004) 274–280
- [2-70] G. N. van den Hoven, A. Polman, C. van Dam, J. W. M. van Uffelen, and M. K. Smith, "Net optical gain at 1.53 μm in Er-doped Al₂O₃ waveguides on silicon," *Applied Physics Letters*, 68 (1996) 1886–1888
- [2-71] G. N. van den Hoven, E. Snoeks, A. Polman, C. van Dam, J.W. M. van Uffelen, and M. K. Smit, "Upconversion in Er-implanted Al₂O₃ waveguides," *J. Appl. Phys.* 79, 1258–1266 (1996).
- [2-72] C. Urlacher, C. Marco de Lucas, E. Bernstein, B. Jacquier, and J. Mugnier, "Study of erbium doped ZrO₂ waveguides elaborated by a sol-gel process", *Optical Materials*, 12 (1999) 19–25
- [2-73] Ross Schermer, Carol Ford, Randy Ramberg, and Anand Gopinath, "Optical amplification at 1534 nm in Er-doped Zirconia Waveguides", *IEEE Journal of Quantum Electronics*, 39 1 (2003) 154–159
- [2-74] Albert Polman, Frank C., and J. M. van Veggel, "Broadband sensitizers for erbium-doped planar optical amplifiers: review", *Journal of Optical Society of America B*, 21 (2004) 871–892
- [2-75] Jung H. Shin, G. N. van den Hoven, and A. Polman, "Direct experimental evidence for trap-state mediated excitation of Er³⁺ in silicon", *Applied Physics Letters*, 67 (1995) 377–379
- [2-76] S. Coffa, G. Franzo', F. Priolo, A. Polman, and R. Serna, "Temperature dependence and quenching processes of the intra-4f luminescence of Er in crystalline Si", *Physical Review B*, 49 16313–16320 (1994)
- [2-77] S. Komuro, S. Maruyama, T. Morikawa, X. Zhao, H. Isshiki, Y. Aoyagi, "Room-temperature luminescence from erbium-doped silicon thin films prepared by laser ablation", *Applied Physics Letters*, 69 (1996) 3896–3898
- [2-78] G. N. van den Hoven, Jung H. Shin, A. Polman, S. Lombardo, and S. U. Campisano, "Erbium in oxygen-doped silicon: optical excitation", *Journal of Applied Physics*, 78 2642–2650 (1995)
-

-
- [2-79] S. Lombardo, S. U. Campisano, G. N. van den Hoven, A. Cacciato, and A. Polman, “Room-temperature luminescence from Er-implanted semi-insulating polycrystalline silicon”, *Applied Physics Letters*, 63 (1993) 1942–1944
- [2-80] S. Lombardo, S. U. Campisano, G. N. van den Hoven, and A. Polman, “Erbium in oxygen-doped silicon: electroluminescence”, *Journal of Applied Physics*, 77 (1995) 6504–6510
- [2-81] J. H. Shin, M. J. Kim, S. Y. Seo, Ch. Lee, “Composition dependence of room temperature 1.54 μm Er^{3+} luminescence from erbium doped silicon:oxygen thin films deposited by electron cyclotron resonance plasma enhanced chemical vapor deposition”, *Materials Research Society Symposium – Proceedings*, 486 (1998) 275-280
- [2-82] F. Iacona, G. Franzo, V. Vinciguerra, A. Irrera, F. Priolo, “Influence of the spatial arrangement on the quantum confinement properties of Si nanocrystals”, *Optical Materials* 17 (2001) 51-55
- [2-83] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, and K. Yamamoto, “1.54- μm photoluminescence of Er^{3+} doped into SiO_2 films containing Si nanocrystals: evidence for energy transfer from Si nanocrystals to Er^{3+} ”, *Applied Physics Letters*, 71 (1997) 1198–1200
- [2-84] M. Fujii, K. Imakita, K. Watanabe, and S. Hayashi, “Coexistence of two different energy transfer processes in SiO_2 films containing Si nanocrystals and Er”, *Journal of Applied Physics*, 95 (2004) 272-280
- [2-85] Oleksandr Savchyn and Pieter G. Kik, Ravi M. Todi and Kevin R. Coffey, “Effect of hydrogen passivation on luminescence-center-mediated Er excitation in Si-rich SiO_2 with and without Si nanocrystals”, *Physical Review B*, 77 (2008) 205438 (1-11)
- [2-87] G. Franzò, S. Boninelli, D. Pacifici, F. Priolo, F. Iacona and C. Bongiorno, “Sensitizing properties of amorphous Si clusters on the 1.54- μm luminescence of Er in Si-rich SiO_2 ” *Applied Physics Letters*, 82 (2003) 2871-3873
- [2-88] F. Lenz, R. DeCorby, A. Meldrum, “Sensitization efficiencies in Er-doped SiO_x films containing amorphous or crystalline silicon nanoclusters”, *Physica Status Solidi* (2008) A 206, 989–992 (2009)
- [2-89] G. Wora Adeola, H. Rinnert, P. Miska, and M. Vergnat, “Influence of the annealing temperature on the photoluminescence of Er-doped SiO thin films”, *Journal of Applied Physics*, 102 (2007) 053515(1-6)
- [2-90] Giorgia Franzo, Emanuele Pecora, Francesco Priolo, and Fabio Iacona, “Role of the Si excess on the excitation of Er doped SiO_x ”, *Applied Physics Letters*, 90 (2007) 183102(1-3)
- [2-91] A. Kanjilal, L. Rebohle, M. Voelskow, W. Skorupa, and M. Helm, “Influence of annealing on the Er luminescence in Si-rich SiO_2 layers coimplanted with Er ions”, *Journal of Applied Physics*, 104, (2008) 103522(1-9)
- [2-92] Ji-Hong Jhe, Jung H. Shin, Kyung Joong Kim, and Dae Won Moon, “The characteristic carrier–Er interaction distance in Er-doped a-Si/ SiO_2 superlattices formed by ion sputtering”, *Applied Physics Letters*, 82 (2003) 4489-4491
- [2-93] C. Garcia, P. Pellegrino, Y. Lebour, B. Garrido, F. Gourbilleau, R. Rizk, “Maximum fraction of Er^{3+} ions optically pumped through Si nanoclusters”, *Journal of Luminescence*, 121 (2006) 204-208
- [2-94] B. Garrido, C. García, S. -Y. Seo, P. Pellegrino, D. Navarro-Urrios, N. Daldosso, L. Pavesi, F. Gourbilleau and R. Rizk, “Excitable Er fraction and quenching phenomena in Er-doped SiO_2 layers containing Si nanoclusters”, *Physical Review B*, 76 (2007) 245308(1-15)
- [2-95] K. Watanabe, M. Fujii, and S. Hayashi, “Resonant excitation of Er^{3+} by the energy transfer from Si nanocrystals”, *Journal of Applied Physics*, 90 (2001) 4761-4767
-

-
- [2-96] F. Gourbilleau, M. Levalois, C. Dufour, J. Vicens, and R. Rizk, "Optimized conditions for an enhanced coupling rate between Er ions and Si nanoclusters for an improved 1.54-mm emission", *Journal of Applied Physics*, 95 (2004) 3717-3722
- [2-97] V. Kapaklis, C. Politis, P. Pouloupoulos, P. Schweiss, "Photoluminescent Si nanoparticles embedded in silicon oxide matrix", *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, 124-125 (2005) 475-478
- [2-98] Fabio Iacona, Corrado Bongiorno, Corrado Spinella, Simona Boninelli and Francesco Priolo, "Formation and evolution of luminescent Si nanoclusters produced by thermal annealing of SiO_x films", *Journal of Applied Physics*, (2004) 3723-3732
- [2-99] T. Shimizu-Iwayama D. E. Hole, P. D. Townsend, "Optical properties of interacting Si nanoclusters in SiO₂ fabricated by ion implantation and annealing", *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, 147 (1999) 350-355
- [2-100] Hak-Seung Han, Se-Young Seo, and Jung H. Shin, "Optical gain at 1.54 mm in erbium-doped silicon nanocluster sensitized waveguide", *Applied Physics Letters*, 79 (2001) 4568-4570
- [2-101] N. Daldosso, D. Navarro-Urrios, M. Melchiorri, L. Pavesi, F. Gourbilleau, M. Carrada, and R. Rizk, C. García, P. Pellegrino, B. Garrido, and L. Cognolato, "Absorption cross section and signal enhancement in Er-doped Si nanocluster rib-loaded waveguides", *Applied Physics Letters*, 86 (2005) 261103 (1-3)
- [2-102] D. Kovalev, J. Diener, H. Heckler, G. Polisski, N. Kunzner, and F. Koch, "Optical absorption cross sections of Si nanocrystals", *Physical Review B*, 61 (2000) 4485-4487
- [2-103] Hak-Seung Han, Se-Young Seo, Jung H. Shin, and Namkyoo Park, "Coefficient determination related to optical gain in erbium-doped, silicon-rich silicon oxide waveguide amplifier", *Applied Physics Letters*, 81 (2002) 3720-3722
- [2-104] B. Garrido, C. García, S.-Y. Seo, and P. Pellegrino, D. Navarro-Urrios, N. Daldosso, and L. Pavesi, F. Gourbilleau and R. Rizk, "Excitable Er fraction and quenching phenomena in Er-doped SiO₂ layers containing Si nanoclusters", *Physical Review B*, 76 (2007) 245308(1-15)
- [2-105] B. Garrido, C. García, P. Pellegrino, D. Navarro-Urrios, N. Daldosso, L. Pavesi, F. Gourbilleau, and R. Rizk, "Distance dependent interaction as the limiting factor for Si nanocluster to Er energy transfer in silica", *Applied Physics Letters*, 89 (2006) 163103
- [2-106] F. Iacona, D. Pacifici, A. Irrera, M. Miritello, G. Franzo, F. Priolo, D. Sanfilippo, G. Di Stefano, and P. G. Fallica, "Electroluminescence at 1.54 mm in Er-doped Si nanocluster-based devices", *Applied Physics Letters*, 81 (2002) 3242-3244
- [2-107] J. M. Sun, W. Skorupa, T. Dekorsy, M. Helm, and A. N. Nazarov, "On the mechanism of electroluminescence excitation in Er-doped SiO₂ containing silicon nanoclusters", *Optical Materials*, 27 (2005) 150-154
- [2-108] Fabio Iacona, Alessia Irrera, Giorgia Franzo, Domenico Pacifici, Isodiana Crupi, Maria Miritello, Calogero D. Presti, and Francesco Priolo, "Silicon based light-emitting devices: properties and applications of crystalline, amorphous, and Er-doped nanoclusters", *IEEE Journal of Selected Topics in Quantum Electronics*, 12 (2006) 1596-1604.
- [2-109] G. Z. Ran, Y. Chen, F.C. Yuan, Y. P. Qiao, J.S. Fu, Z. C. Ma, W.H. Zong, and G. G. Qin, "An effect of Si nanoparticles on enhancing Er³⁺ electroluminescence in Si-rich SiO₂:Er films", *Solid State Communications*, 118 (2001) 599-602
- [2-110] J. Shakya, K. H. Kim, J. Y. Lin, and H. X. Jiang, "Enhanced light extraction in III-nitride ultraviolet photonic crystal light-emitting diodes", *Applied Physics Letters*, 85 (2004) 142-144
-

-
- [2-111] Min-Ki Kwon, Ja-Yeon Kim, Il-Kyu Park, Ki Seok Kim, Gun-Young Jung, Seong-Ju Park, Je Won Kim, and Yong Chun Kim, "Enhanced emission efficiency of GaN/InGaN multiple quantum well light-emitting diode with an embedded photonic crystal", *Applied Physics Letters*, 92 251110 (2008) (1-3)
- [2-112] K. Bergenek, Ch. Wiesmann, R. Wirth, L. O'Faolain, N. Linder, K. Streubel, and T.F. Krauss, "Enhanced light extraction efficiency from AlGaInP thin-film light emitting diodes with photonic crystals", *Applied Physics Letters* 93, 041105 (2008) (1-3)
- [2-113] H. Y. Ryu, Y. H. Lee, R. L. Sellin and D. Bimberg, "Over 30-fold enhancement of light extraction from free-standing photonic crystal slabs with InGaAs quantum dots at low temperature", *Applied Physics Letters* 79, 3573-3575 (2001)
- [2-114] Ja-Yeon Kim, Min-Ki Kwon, Ki-Sung Lee, Seong-Ju Park, Sang Hoon Kim and Ki-Dong Lee "Enhanced light extraction from GaN-based green light-emitting diode with photonic crystal", *Applied Physics Letters*, 91 181109 (2007) (1-3)
- [2-115] Ja-Yeon Kim, Seok-In Na, Ga-Young Ha, Min-Ki Kwon, Il-Kyu Park, Jae-Hong Lim, and Seong-Ju Park, "Thermally stable and highly reflective AgAl alloy for enhancing light extraction efficiency in GaN light-emitting diodes", *Applied Physics Letters*, 88 (2006) 043507(1-3)
- [2-116] Jong Kyu Kim, Thomas Gessmann, Hong Luo, and E. Fred Schubert, "GaInN light-emitting diodes with RuO₂/SiO₂/Ag omni-directional reflector", *Applied Physics Letters*, 84 (2004) 4508-4510
- [2-117] Chul Huh, Kug-Seung Lee, Eun-Jeong Kang, and Seong-Ju Park, "Improved light-output and electrical performance of InGaN-based light-emitting diode by microroughening of the p-GaN surface", *Journal of Applied Physics*, 93(2003) 9383
- [2-118] Seok-In Na, Ga-Young Ha, Dae-Seob Han, Seok-Soon Kim, Ja-Yeon Kim, Jae-Hong Lim, Dong-Joon Kim, Kyeong-Ik Min, and Seong-Ju Park, "Selective wet etching of p-GaN for efficient GaN-based light-emitting diodes", *IEEE Photonics Technology Letters*, 18 (2006) 1512-1514
- [2-119] I. Schnitzer, E. Yablonovitch, C. Caneau, T. J. Gmitter, and A. Scherer, "30% external quantum efficiency from surface textured, thin-film light emitting diodes", *Applied Physics Letters*, 63 (1993) 2174-2176
- [2-120] E. F. Schubert, N. E. J. Hunt, M. Micovic, R. J. Malik, D. L. Sivco, A. Y. Cho, and G. J. Zydzik, "Highly Efficient Light-Emitting Diodes with Microcavities", *Science*, 265 (1994) 943-945
- [2-120] Ja-Yeon Kim, Min-Ki Kwon, Jae-Pil Kim, and Seong-Ju Park, "Enhanced Light Extraction From Triangular GaN-Based Light-Emitting Diodes", *IEEE Photonics Technology Letters*, 19 (2007) 1865-1867
- [2-121] Shanhui Fan, Pierre R. Villeneuve, and J. D. Joannopoulos, and E. F. Schubert, "High Extraction Efficiency of Spontaneous Emission from Slabs of Photonic Crystals", *Physical Review Letters*, 78 (1997) 3294-3297
- [2-122] Fang-Fang 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/SiO₂ multilayers via in-plane modulation of photonic crystal patterns", *Applied Physics Letters*, 93 091901 (1-3) (2008)
- [2-123] Sang Hoon Kim, Ki-Dong Lee, Ja-Yeon Kim, Min-Ki Kwon and Seong-Ju Park, "Fabrication of photonic crystal structures on light emitting diodes by nanoimprint lithography", *Nanotechnology*, 18 (2007) 055306(1-5)
-

-
- [2-124] C. Qian, Z. -X. Zhang, F. Zhang, C. -L. Lin, "Effect of implantation dose and annealing time on the formation of Si nanocrystals embedded in thermal oxide", *Materials Research Society Symposium Proceedings*, 1020 (2007) 195-200
- [2-125] J. Linnros, N. Lalic, A. Galeckas, and V. Grivickas, "Analysis of the stretched exponential photoluminescence decay from nanometer-sized silicon crystals in SiO₂", *Journal of Applied Physics*, 86 (1999) 6128-6134
- [2-126] J. G. Zhu, C. W. White, J. D. Budai, S. P. Withrow, and Y. Chen, "Growth of Ge, Si, and SiGe nanocrystals in SiO₂ matrices", *Journal of Applied Physics*, 78 (1995) 4386-4389
- [2-127] C. Bonafos, M. Carrada, N. Cherkashin, H. Coffin, D. Chassaing, G. Ben Assayag, A. Claverie, T. Muller, K.H. Heinig, M. Perego, M. Fanciulli, P. Dimitrakis, and P. Normand, "Manipulation of two-dimensional arrays of Si nanocrystals embedded in thin SiO₂ layers by low energy ion implantation", *Journal of Applied Physics*, 95 (2004) 5696-5702
- [2-128] Tsutomu Shimizu-Iwayama, Katsunori Fujita, Setsuo Nakao, Kazuo Saitoh, Tetsuo Fujita, and Noriaki Itoh, "Visible photoluminescence in Si⁺-implanted silica glass", *Journal of Applied Physics*, 75 (1994) 7779-7783
- [2-129] K. S. Min, K. V. Shcheglov, C. M. Yang, H. A. Atwater, M. L. Brongersma, and A. Polman, "Defect-related versus excitonic visible light emission from ion beam synthesized Si nanocrystals in SiO₂", *Applied Physics Letters*, 69 (1996) 2033-2035
- [2-130] Y. Q. Wang, G. L. Kong, W. D. Chen, H. W. Diao, C. Y. Chen, S. B. Zhang, and X. B. Liao, "Getting high-efficiency photoluminescence from Si nanocrystals in SiO₂ matrix", *Applied Physics Letters*, 81 (2002) 4174-4176
- [2-131] M. Bedjaoui, B. Despax, M. Caumont, and C. Bonafos, "Si nanocrystal-containing SiO_x (x < 2) produced by thermal annealing of PECVD realized thin films", *Materials Science and Engineering B*, 124-125 (2005) 508-512
- [2-132] Fabio Iacona, Giorgia Franzo, and Corrado Spinella, "Correlation between luminescence and structural properties of Si nanocrystals", *Journal of Applied Physics*, 87 (2000) 1295-1303
- [2-133] Ching-Song Yang, Chrong-Jung Lin, Ping-Yu Kuei, Sheng-Fu Horng, Charles Ching-Hsiang Hsu, and Ming-Chi Liaw, "Quantum size effects on photoluminescence from Si nanocrystals in PECVD silicon-rich-oxide", *Applied Surface Science*, 113/114 (1997) 116-120
- [2-134] Li Wei-Long, Jia Rui, Liu Ming, Chen Chen, Xie Chang-Qing, Zhu Chen-Xin, Li Hao-Feng, Zhang Pei-Wen, Ye Tian-Chun, "Fabrication and Characterization of Si Nanocrystals Synthesized by Electron Beam Evaporation of Si and SiO₂ Mixture", *Chinese Physics Letters*, 26 (2009) 046801(1-4)
- [2-135] A. Barranco, F. Yubero and J. P. Espinos. F. Groening, A. R. Gonzales-Elipe, "Electronic state characterization of SiO_x thin films prepared by evaporation", *Journal of Applied Physics*, (2005) 97, 113714(1-8)
- [2-136] H. Morisaki, F. W. Ping, H. Ono, and K. Yazawa, "Above-band-gap photoluminescence from Si fine particles with oxide shell", *Journal of Applied Physics*, 70 (1991) 1869-1870
- [2-137] D. Nesheva, C. Raptis, A. Perakis, I. Bineva, Z. Aneva, Z. Levi, and S. Alexandrova, and H. Hofmeister, "Raman scattering and photoluminescence from Si nanoparticles in annealed SiO_x thin films", *Journal of Applied Physics*, 92 (2002) 4678-4683
- [2-138] H. Rinnert, M. Vergnat, G. Marchal, and A. Burneau, "Strong visible photoluminescence in amorphous SiO_x and SiO_x : H thin films prepared by thermal evaporation of SiO powder", *Journal of Luminescence*, 80 (1999) 445-448
- [2-139] E. Edelberg, S. Bergh, R. Naone, M. Hall, and E.S. Aydil, "Luminescence from plasma deposited silicon films", *Journal of Applied Physics*, 81 (1997) 2410-2417
-

-
- [2-140] R.K. Soni, L.F. Fonseca, O. Resto, M. Buzaianu, and S.Z. Weisz, "Size-dependent optical properties of silicon nanocrystals", *Journal of Luminescence*, 83-84 (1999) 187-191
- [2-141] S. Hayashi and K. Yamamoto, "Optical properties of Si-rich SiO₂ films in relation with embedded Si mesoscopic particles", *Journal of Luminescence*, 70 (1996) 352-363
- [2-142] Li-ping You, C.L. Heng, S. Y. Ma, Z. C. Ma, W. H. Zong, Zh. Wu, and G. G. Qin, "Precipitation and crystallization of nanometer Si clusters in annealed Si-rich SiO₂ films", *Journal of Crystal Growth*, 212 (2000) 109 -114
- [2-143] Y. He, L. Bi, J. Y. Feng, and Q. L. Wu, "Properties of Si-rich SiO₂ films by RF magnetron sputtering", *Journal of Crystal Growth*, 280 (2005) 352-356
- [2-144] [2-115] E. Werwa, A. A. Seraphin, L. A. Chin, Chuxin Zhou, and K. D. Kolenbrander, "Synthesis and processing of silicon nanocrystallites using a pulsed laser ablation supersonic expansion method", *Applied Physics Letters*, 64 (1994) 1821-1823
- [2-145] [2-116] L. N. Dinh, L. L. Chase, M. Balooch, L. J. Terminello, and F. Wooten, "Photoluminescence of oxidized silicon nanoclusters deposited on the basal plane of graphite", *Applied Physics Letters*, 65 (1994) 3111-3113
- [2-146] J. M. Sun, W. Skorupa, T. Dekorsy, M. Helm, A. N. Nazarov, "On the mechanism of electroluminescence excitation in Er-doped SiO₂ containing silicon nanoclusters", *Optical Materials*, 27 (2005) 1050-1054
- [2-147] C. S. Zhang, J. Z. Sun, X. Wang, F. Zhang, "Influence of thermal treatment on photoluminescence of Er-doped Si-rich SiO₂ prepared by ion implantation", *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, 242 (2006) 279-281
- [2-148] C. S. Zhang, J. Z. Sun, and F. Zhang, "Structure and composition evolutions of Er-doped Si-rich SiO₂ film under annealing", *Microelectronic Engineering*, 81 (2005) 378-381
- [2-149] B. Maiti, and J.C. Lee, "Low-pressure chemical-vapor-deposited silicon-rich oxides for nonvolatile memory applications", *Electronic Device Letters*, 13 (1992) 624-626
- [2-150] N. Daldosso, G. Das, S. Larcheri, G. Mariotto, G. Dalba, L. Pavesi, A. Irrera, F. Priolo, F. Iacona, and F. Rocca, "Silicon nanocrystal formation in annealed silicon-rich silicon oxide films prepared by plasma enhanced chemical vapor deposition", *Journal of Applied Physics*, 101 (2007) 113510 (1-7)
- [2-151] A. Morales, J. Barreto, C. Dominguez, M. Riera, M. Aceves, and J. Carrillo, "Comparative study between silicon-rich oxide films obtained by LPCVD and PECVD", *Physica E, Low-dimensional Systems and Nanostructures*, 38 (2007) 54-58
- [2-152] Konstantinos Koukos, Elena Bedel-Pereira, Olivier Gauthier-Lafaye, Emmanuel Scheid, Laurent Bouscayrol, Bernard Franc, Philippe Arguel, Sophie Bonnefont, Francoise Lozes-Dupuy, and Gerard Sarraeyrouse, "Effect of Annealing Conditions on Photoluminescence Properties of Low-Pressure Chemical Vapour Deposition-Grown Silicon Nanocrystals", *Japanese Journal of Applied Physics*, 47 (2008) 130-132
- [2-153] C. L. Heng, O. H. Y. Zalloum, J. Wojcik, T. Roschuk, and P. Mascher, "On the effects of double-step anneal treatments on light emission from Er-doped Si-rich silicon oxide", *Journal of Applied Physics*, 103 (2008) 024309(1-9)
- [2-154] J. Heitmann, M. Schmidt, M. Zacharias, V. Yu, Timoshenko, M. G. Lisachenko, and P. K. Kashkarov, "Fabrication and photoluminescence properties of erbium doped size-controlled silicon nanocrystals", *Materials Science and Engineering B*, 105 (2003) 214-220
- [2-155] Kiyotaka Wasa, and Shigeru Hayakawa, Shigeru Haber, "Handbook of Sputter Deposition Technology: Principles, Technology, and Applications", William Andrew Publishing (1992)
-

-
- [2-156] J. P. Zhang, L. D. Zhang, L.Q. Zhu, Y. Zhang, M. Liu, X.J. Wang, G. He, "Characterization of ZnO:N films prepared by annealing sputtered zinc oxynitride films at different temperatures", *Journal of Applied Physics*, 102 (2007) 114903
- [2-157] J.H. Lee, J.S. Choi, S. Hong, I. Hwang, Y.-I. Kim, S.J. Anh, S.-O. Kang, B.H. Park, "Fabrication and memory effect of Zr nanocrystals embedded in ZrO₂ dielectric layer", *Japanese Journal of Applied Physics*, 46 (2007) L1246-L1248
- [2-158] J. Xu, J. Tao, Z. Chen, W. Zhu, S. Jiang, Z. Xu, "Preparation of Ni-Cu-Mo-Cr film deposited on AZ31magnesium alloy by double glow sputtering with Cu interlayer", *Surface and Coatings Technology*, 202 (2007) 577-582
- [2-159] H. Murata, T. Ohba, "Microstructure and electrical property of sputtered Cr-Mo thin films", *Materials Transactions*, 49 (2008) 2907-2911
- [2-160] X. L. Meng, M. Sato, A. Ishida, "Structure of martensite in sputter-deposited (Ni,Cu)-rich Ti-Ni-Cu thin films containing Ti(Ni,Cu)₂ precipitates" *Acta Materialia*, 57 (2009) 1525-1535
- [2-161] S. -Y. Lee, S. -C. Wang, J. -S. Chen, J. -L. Huang, "Effects of nitrogen partial pressure on electrical properties and thermal stability of TiAlN films by ion beam sputter deposition", *Surface and Coatings Technology*, 202 (2007) 977-981
- [2-162] S. Jang, B.S. Kang, F. Ren, N.W. Emanetoglu, H. Shen, W.H. Chang, B. P. Gila, S. J. Pearton, "Comparison of e-beam and sputter-deposited ITO films for 1.55 μ m Metal-Semiconductor-Metal photo-detector applications", *ECS Transactions*, 6 (2007) 59-67
- [2-163] J. U. Schmidt, and B. Schmidt, "Investigation of Si nanocluster formation in sputter-deposited silicon sub-oxides for nanocluster memory structures", *Materials Science and Engineering B: Solid-State Materials for Advanced Technology* 101 (2003) 28-33
- [2-164] F. Gourbilleau, R. Madelon, C. Dufour, R. Rizk, "Fabrication and optical properties of Er-doped multilayers Si-rich SiO₂/SiO₂: Size control, optimum Er-Si coupling and interaction distance monitoring", *Optical Materials* 27 (2005) 868-875
- [2-165] K. Hijazi, L. Khomenkova, J. Cardin, F. Gourbilleau, R. Rizk, "Structural and optical characteristics of Er-doped SRSO layers deposited by the confocal sputtering technique", *Physica E: Low-Dimensional Systems and Nanostructures* 41 (2009) 1067-1070
- [2-166] G. R. Lin, C. J. Lin, C. Y. Chen, "Enhanced pumping energy transfer between Si nanocrystals and erbium ions in Si-rich SiO_x sputtered using Si/Er₂O₃ encapsulated SiO substrate", *Journal of Nanoscience and Nanotechnology*, 7 (2007) 2847-2851
- [2-167] Leonid Khriachtchev, Olli Kilpela, Suvi Karirinne, Jaako Keranen, Toivo Lepisto, "Substrate dependent crystallization and enhancement of visible photoluminescence in thermal annealing of Si/SiO₂ superlattices", *Applied Physics Letters*, 78 (2001) 323-325
- [2-168] M. Lopez, B. Garrido, C. Garcia, P. Pellegrino, A. Perez-Rodriguez, J. R. Morante, C. Bonafos, M. Carrada, and A. Claverie, "Elucidation of the surface passivation role on the photoluminescence emission yield of silicon nanocrystals embedded in SiO₂", *Applied Physics Letters*, 80 (2002) 1637-1639
- [2-169] Annett Thogersen, Jeyanthinath Mayandi, Terje G. Finstad, Arne Olsen, Jens Sherman Christensen, Masanori Mitome, and Yoshio Bando, "Characterization of amorphous and crystalline silicon nanoclusters in ultrathin silica layers", *Journal of Applied Physics*, 104 (2008) 094315(1-7)
- [2-170] Jiun-Lin Yeh, Hsuen-Li Chen, An Shih, Si-Chen Lee, "Formation of Si nanoclusters in amorphous silicon thin films by excimer laser annealing", *Electronics Letters* 35 (1999) 2058-2059
-

-
- [2-171] Anuranjita Tewary, Rohan D. Kekatpure, and Mark L. Brongersma, "Controlling defect and Si nanoparticle luminescence from silicon oxynitride films with CO₂ laser annealing", *Applied Physics Letters*, 88 (2006) 093114 (1-3)
- [3-1] G. L. Tan, M. F. Lemon, D. J. Jones, and R. H. French, "Optical properties and London dispersion interaction of amorphous and crystalline SiO₂ determined by vacuum ultraviolet spectroscopy and spectroscopic ellipsometry", *Physical Review B*, 72 (2005) 205117(1-9)
- [3-2] Andy C. Van Popta, June Cheng, Jeremy C. Sit, and Michael J. Brett, "Birefringence enhancement in annealed TiO₂ thin films", *Journal of Applied Physics*, 102 (2007) 013517 (1-7)
- [3-3] D. Nesheva, N. Nedev, Z. Levi, R. Bruggemann, E. Manolov, K. Kirilov, and S. Meier, "Absorption and transport properties of Si rich oxide layers annealed at various temperatures", *Semiconductor Science and Technology*, 23 (2008) 045015-0.45022
- [3-4] Agilent 8453 UV-Vis spectroscopy system manual
- [3-5] M. Ocana, V. Fornes, C. J. Serna, "The variability of the infrared power spectrum of amorphous SiO₂", *Journal of Non-crystalline Solids*, 107 (1989) 187-192
- [3-6] Gan Fuxi, "*Optical and spectroscopic properties of glasses*", Berlin: Springer Verlag (1992)
- [3-7] N. Daldosso, G. Das, S. Larcheri, G. Marriotto, G. Dalba, L. Pavesi, A. Irrera, F. Priolo, F. Iacona, and F. Rocca, "Silicon nanocrystal formation in annealed silicon-rich silicon oxide films prepared by plasma enhanced chemical vapour deposition", *Journal of Applied Physics*, 101 (2007) 113510(1-7)
- [3-8] F. Ay, and A. Aydinli, "Comparative investigation of hydrogen bonding in silicon based PECVD grown dielectrics for optical waveguides", *Optical Materials*, 26 (2004) 33-46
- [3-9] Pelkin Elmer FTIR manual
- [3-10] Manual J. A. Woollam
- [3-11] Ching-Song Yang, Chrong-Jung Lin, Ping-Yu Kuei, Sheng-Fu Horng, Charles Ching-Hsiang Hsu, and Ming-Chi Liaw, "Quantum size effects on photoluminescence from Si nanocrystals in PECVD silicon-rich-oxide", *Applied Surface Science*, 113/114 (1997) 116-120
- [3-12] T. S. Iwayama, T. Hama, D. E. Hole, I. W. Boyd, "Enhanced luminescence from encapsulated silicon nanocrystals in SiO₂ with rapid thermal anneal", *Vacuum*, 81 (2006) 179-185
- [3-13] Anuranjita Tewary, Rohan D. Kekatpure, and Mark L. Brongersma, "Controlling defect and Si nanoparticle luminescence from silicon oxynitride films with CO₂ laser annealing", *Applied Physics Letters*, 88 (2006) 093114 (1-3)
- [3-14] Jobin Yvon Fluorolog-3 Manual
- [3-15] J. Heitmann, M. Schmidt, M. Zacharias, V. Yu, Timoshenko, M.G. Lisachenko, and P.K. Kashkarov, "Fabrication and photoluminescence properties of erbium doped size-controlled silicon nanocrystals", *Materials Science and Engineering B*, 105 (2003) 214-220
- [3-16] Maria Makarova, Vanessa Sih, Joe Warga, Rui Li, Luca Dal Negro, and Jelena Vuckovic, "Enhanced light emission in photonic crystal nanocavities with Erbium-doped silicon nanocrystals", *Applied Physics Letters*, 92 (2008) 161107(1-3)
- [3-17] Fang-Fang Ren, M.B. Yu, J. D. Y, Q. Chen, S. T. Tan, G.Q. Lo, and D. L. Kwong, "Strong vertical light output from thin silicon rich oxide/SiO₂ multilayers via in-plane modulation of photonic crystal patterns", *Applied Physics Letters*, 93 (2008) 091901
- [3-18] Micro-Raman PL Manual
-

-
- [3-19] M. L. Brongersma, A. Polman, K. S. Min, E. Boer, T. Tambo, and H. A. Atwater, "Tuning the emission wavelength of Si nanocrystals in SiO₂ by oxidation", *Applied Physics Letters*, 72 (1998) 2577-2579
- [3-20] Ji-Hong Jhe, Jung H. Shin, Kyung Joong Kim, and Dae Won Moon, "The characteristic carrier-Er interaction distance in Er-doped a-Si/SiO₂ superlattices formed by ion sputtering", *Applied Physics Letters*, 82 (2003) 4489-4491
- [3-21] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, and K. Yamamoto, "1.54-μm photoluminescence of Er³⁺ doped into SiO₂ films containing Si nanocrystals: evidence for energy transfer from Si nanocrystals to Er³⁺", *Applied Physics Letters*, 71 (1997) 1198-1200
- [3-22] L. X. Yi, J. Heitmann, R. Scholz and M. Zacharias, "Phase separation of thin SiO layers in amorphous SiO/SiO₂ superlattices during annealing", *Journal of Physics: Condensed Matter*, 15 (2003) S2887-S2895
- [3-23] An-Thung Cho, Jia-Min Shieh, Jiann Shieh, Yi-Fan Lai, Bau-Tong Dai, Fu-Ming Pan, Hao-Chung Kuo, Yong-Chang Lin, Kuei-Jung Chao, and Pang-Hung Liu, "Emission of bright blue light from mesoporous Silica with dense Si (Ge) nanocrystals", *Electrochemical and Solid-State Letters*, 8 (2005) G143-G146
- [3-24] JEOL Transmission Electron Microscopy (TEM) manual
- [3-25] Siemens D5005 XRD manual
- [3-26] Kiyotaka Wasa, and Shigeru Hayakawa, Shigeru Haber, "Handbook of Sputter Deposition Technology: Principles, Technology, and Applications", William Andrew Publishing (1992)
- [3-27] Y. Naka, N. Yamamoto, M. Kishi, D. Miyakawi, T. Yoshida, T. Minami, K. Ito, M. Tsuchiya, and Y. Nakamura, "Optical characterization and X-ray photoelectron spectroscopy of erbium-doped silicon suboxide infrared emitting at 1.5 μm", *Japanese Journal of Applied Physics* 47 (2008) 8871-8873
- [3-28] E. Quiroga, W. Bensch, Z. Yu, M. Aceves, R. A. De Souza, M. Martin, V. Zaporozhchenko, and F. Faupel, "Structural characteristics of a multilayer of silicon rich oxide (SRO) with high Si content prepared by LPCVD", *Physica Status Solidi (A) Applications and Materials*, 206 (2009) 263-269
- [3-29] X-ray Photoelectron Spectroscopy manual
- [3-30] Dektak Surface Profiler Manual
- [3-31] JEOL Scanning electron microscopy (SEM) manual
- [3-32] H. P. Weber, F. A. Dunn, W. N. Leibolt, "Loss measurements in thin-film optical waveguides", *Applied Optics*, 12 (1973) 755-757
- [3-33] R. Ulrich, "Theory of the prism-film coupler by plane wave analysis", *Journal of the Optical Society of America*, 60 (1970), 1337-1350
- [3-34] Metricon Prism coupler manual
-
- [4-1] F. Iacona, G. Franzo, V. Vinciguerra, A. Irrera, F. Priolo, "Influence of the spatial arrangement on the quantum confinement properties of Si nanocrystals", *Optical Materials* 17 (2001) 51-55
- [4-2] Johannes Heitmann, Frank Muller, Lixin Yi, and Margit Zacharias, Dmitri Kovalev, and Frank Eichhorn, "Excitons in Si nanocrystals: Confinement and migration effects", *Physical Review B*, 69 (2004) 195309 (1-7)
-

-
- [4-3] K. Watanabe, M. Fujii, and S. Hayashi, "Resonant excitation of Er^{3+} by the energy transfer from Si nanocrystals", *Journal of Applied Physics*, 90 (2001) 4761-4767
- [4-4] M. Luppi, and S. Ossicini, "Ab initio study on oxidized silicon clusters and silicon nanocrystals embedded in SiO_2 : Beyond the quantum confinement effect *Physical Review B - Condensed Matter and Materials Physics*, 71 (2005) 1-15
- [4-5] M. Nishida, "Electronic state calculations of Si quantum dots: oxidation effects", *Physical Review B - Condensed Matter and Materials Physics*, 69 (2004) 165324 (1-5)
- [4-6] G. Allan, C. Delerue, and M. Lannoo, "Electronic Structure of Amorphous Silicon Nanoclusters", *Physical Review Letters*, 78 (1997) 3161-3164
- [4-7] A. Barranco, F. Yubero and J. P. Espinos. F. Groening, A. R. Gonzales-Elipé," Electronic state characterization of SiO_x thin films prepared by evaporation", *Journal of Applied Physics*, (2005) 97, 113714(1-8)
- [4-8] U. Kahler and H. Hofmeister, "Visible light emission from Si nanocrystalline composites via reactive evaporation of SiO", *Optical Materials*, 17 (2001) 83-86
- [4-9] R. K. Soni, L. F. Fonseca, O. Resta, M. Buzaianu, and S. Z. Weisz, "Size-dependent optical properties of silicon nanocrystals", *Journal of Luminescence*, 83-84 (1999) 187-191
- [4-10] S. K. Bera, S. Chaudhuri, A. K. Bandyopadhyay, B. R. Chakraborty, and A. K. Pal, *Journal of Physics D: Applied Physics*, "Quantum size effect in silicon nanocrystals prepared by dc magnetron sputtering", 34 (2001) 273-278
- [4-11] M. Zhu, Y. Han, R.B. Wehrspohn, and D. Ballutaud, "The origin of visible photoluminescence from silicon oxide thin films prepared by dual-plasma chemical vapor deposition", *Journal of Applied Physics*, 83 (1998) 5386-5393
- [4-12] F. Iacona, G. Franzo, and C. Spinella, "Correlation between luminescence and structural properties of Si nanocrystals", *Journal of Applied Physics* 87 (2000) 1295-1303
- [4-13] J. Linnros, N. Lalic, A. Galeckas, and V. Grivickas, "Analysis of the stretched exponential photoluminescence decay from nanometer-sized silicon crystals in SiO_2 ", *Journal of Applied Physics*, 86 (1999) 6128-6133
- [4-14] M. Zacharias, J. Heitmann, R. Scholz, and U. Kahler, M. Schmidt, and J. Blasing, "Size-controlled highly luminescent silicon nanocrystals: A SiO/SiO_2 superlattice approach", *Applied Physics Letters*, 80 (2002) 661-663
- [4-15] N. Daldosso, G. Das, S. Larcheri, G. Mariotto, G. Dalba, L. Pavesi, A. Irrera, F. Priolo, F. Iacona, and F. Rocca," Silicon nanocrystal formation in annealed silicon-rich silicon oxide films prepared by plasma enhanced chemical vapor deposition", *Journal of Applied Physics*, 101 (2007) 113510(1-7)
- [4-16] L. X. Yi, J. Heitmann, R. Scholz, and M. Zacharias, "Si rings, Si clusters, and Si nanocrystals-different states of ultrathin SiO_x layers", *Applied Physics Letters*, 81 (2002) 4248-4250
- [4-17] F. Gourbilleau, X. Portier, C. Ternon, P. Voivenel, R. Madelon, and R. Rizk, "Si-rich/ SiO_2 nanostructured multilayers by reactive magnetron sputtering", *Applied Physics Letters*, 78 (2001) 3058-3060
- [4-18] Konstantinos Koukos, Elena Bedel-Pereira, Olivier Gauthier-Lafaye, Emmanuel Scheid, Laurent Bouscayrol, Bernard Franc, Philippe Arguel, Sophie Bonnefont, Francoise Lozes-Dupuy, and Gerard Sarrabayrouse, "Effect of Annealing Conditions on Photoluminescence Properties of Low-Pressure Chemical Vapour Deposition-Grown Silicon Nanocrystals", *Japanese Journal of Applied Physics*,. 47 (2008) 130-132
-

-
- [4-19] Daigil Cha, Jung H. Shin, In-Hyuk Song and Min-Koo Han, "Enhanced formation of luminescent nanocrystal Si embedded in SiO/SiO₂ superlattice by excimer laser irradiation", *Applied Physics Letters*, 84 (2004) 1287-1289
- [4-20] Jiun-Lin Yeh, Hsuen-Li Chen, An Shih, Si-Chen Lee, "Formation of Si nanoclusters in amorphous silicon thin films by excimer laser annealing", *Electronics Letters* 35 (1999) 2058-2059
- [4-21] M. Lopez, B. Garrido, C. Garcia, P. Pellegrino, A. Perez-Rodriguez, J. R. Morante, C. Bonafos, M. Carrada, and A. Claverie, "Elucidation of the surface passivation role on the photoluminescence emission yield of silicon nanocrystals embedded in SiO₂", *Applied Physics Letters*, 80 (2002) 1637-1639
- [4-22] M.V. Wolkin, J. Jornie, P. M. Fauchet, G. Allan, C. Delerue, "Electronic States and Luminescence in Porous Silicon Quantum Dots: The Role of Oxygen", *Physical Review Letters*, 82 (1999) 197-200
- [4-23] Leonid Khriachtchev, Olli Kilpela, Suvi Karirinne, Jaako Keranen, Toivo Lepisto, "Substrate dependent crystallization and enhancement of visible photoluminescence in thermal annealing of Si/SiO₂ superlattices", *Applied Physics Letters*, 78 (2001) 323-325
- [4-24] S. Godefroo, M. Hayne, M. Jivanescu, A. Stesmans, M. Zacharias, O. I. Lebedev, G. Van Tendeloo, and V. V. Moshchalkov, "Classification and control of the origin of photoluminescence from Si nanocrystals", *Nature Nanotechnology*, 3 (2008) 174-178
- [4-25] Leonid Khriachtchev, Markku Rasanen, Sergei Novikov, and Lorenzo Pavesi, "Systematic correlation between Raman spectra, photoluminescence intensity, and absorption coefficient of silica layers containing Si nanocrystals", *Applied Physics Letters*, 85 (2004) 1511-1513
- [4-26] Yoshihiko Kanemitsu, Hiroshi Uto, Yasuaki Masumoto, Takahiro Matsumoto, Toshiro Futagi, and Hidenori Mimura, "Microstructure and optical properties of free-standing porous silicon films: Size dependence of absorption spectra in Si nanometer-sized crystallites", *Physical Review B*, 48 (1993) 2827-2830
- [4-27] L. X. Yi, J. Heitmann, R. Scholz, and M. Zacharias, "Phase separation of thin SiO layers in amorphous SiO/SiO₂ superlattices during annealing", *Journal of Physics: Condensed Matters*, 15 (2003) S2887-S2895
- [4-28] Gong-Ru Lin, Chun-Jung Lin, Chi-Kuan Lin, Li-Jen Chou, Yu-Lun Chueh, "Oxygen defect and Si nanocrystal dependent white-light and near-infrared electroluminescence of Si-implanted and plasma-enhanced chemical-vapor deposition-grown Si-rich SiO₂", *Journal of Applied Physics*, 97 (2005) 094306(1-8)
- [4-29] Hiroyuki Nishikawa, Eiki Watanabe, Daisuke Ito, Yuryo Sakurai, Kaya Nagasawa, and Yoshimichi Ohki, "Visible photoluminescence from Si clusters in γ -irradiated amorphous SiO₂", *Journal of Applied Physics*, 80 (1996) 3513-3517
- [4-30] L. Tsybeskov, Ju. V. Vandyshv, and P. M. Fauchet, "Blue emission in porous silicon: Oxygen-related photoluminescence", *Physical Review B*, 49 (1994) 7821-7824
- [4-31] 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*, 66 (1995) 851-853
- [4-32] H. Takagi, H. Owada, Y. Yamazaki, A. Ishizaki, and T. Nakagiri, "Quantum size effects on photoluminescence in ultrafine Si particles", *Applied Physics Letters*, 56 (1990) 2379-2381
- [4-33] Vladimir Svrcek, Takeshi Sasaki, Yoshiki Shimizu, and Naoto Koshizaki, "Blue luminescent silicon nanocrystals prepared by nanosecond laser ablation and stabilized in electronically compatible spin on glasses", *Journal of Applied Physics*, 103 (2008) 023101 (1-8)
-

-
-
- [4-34] A. Podhorodecki, J. Misiewicz, F. Gourbilleau and R. Rizk, "Absorption Mechanisms of Silicon Nanocrystals in Cosputtered Silicon-Rich-Silicon Oxide Films", *Electrochemical and Solid State Letters*, 11 K31 (2008)
- [4-35] P.Y. Yu, M. Cardona, "*Fundamental of Semiconductors, Physics and Materials Properties*", New York: Springer (1996)
- [4-36] M. Lopez, B. Garrido, C. Garcia, P. Pellegrino, A. Perez-Rodriguez, J. R. Morante, C. Bonafos, M. Carrada, and A. Claverie, "Elucidation of the surface passivation role on the photoluminescence emission yield of silicon nanocrystals embedded in SiO₂", *Applied Physics Letters*, 80 (2002) 1637-1639
- [4-37] X. Y. Chen, Y. F. Lu, Y. H. Wu, B. J. Cho, B. J. Yang, T.Y. F. Liwe, "Laser annealing of silicon nanocrystal films prepared by pulsed-laser deposition", *Journal of Vacuum Science and Technology B: Microelectronics and Nanometer Structures*, 22 (2008) 1731-1737
- [4-38] G. S. Fu, W. Yu, S. Q. Li, Y. C. Peng, L Han, "Preparation of nanocrystalline silicon films by excimer laser-induced crystallization", *Proceedings of SPIE - The International Society for Optical Engineering* 4905 (2002) 438-441
-
- [5-1] P. Photopoulos, A. G. Nassiopoulou, D.N. Kouvatsos, and A. Travlos, "Photoluminescence from nanocrystalline silicon in Si/SiO₂ superlattices", *Applied Physics Letters*, 76 (2000) 3588-3590
- [5-2] M. L. Bongersma, A. Polman, K.S. Min, E. Boer, T. Tambo, and H. A. Atwater, "Tuning the emission wavelength of Si nanocrystals in SiO₂ by oxidation", *Applied Physics Letters*, 72 (1998) 2577-2579
- [5-3] Samson T.H. Silalahi, H.Y. Yang, K. Pita, Yu Mingbin, "Rapid Thermal Annealing of Sputtered Silicon-Rich Oxide/SiO₂ Superlattice Structure", *Electrochemical and Solid-State Letters*, 12 (2009) K29-K32
- [5-4] K. C. Sheer, R.A. Rao, R. Muralidhar, S. Bagchi, J. Conner, L. Lozano, C. Perez, M. Sadd, and B.E. White Jr, "Thermal oxidation of silicon nanocrystals in O₂ and NO ambient", *Journal of Applied Physics*, 93 (2003) 5637-5642
- [5-5] D.B. Kao, J. P. McVittie, W.D. Nix, and K.C. Saraswat, "Modeling of stress effects in silicon oxidation", *IEEE Transactions on Electron Devices*, 36 (1989) 2415-2421
- [5-6] 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*, 82 (1999) 197-200.
- [5-7] J. S. Bitten, N. S. Lewis, H. A. Atwater, A. Polman, "Size-dependent oxygen-related electronic states in silicon nanocrystals", *Applied Physics Letters*, 84 (2004) 5389-5391
-
- [6-1] M. Fujii, K. Imakita, K. Watanabe, and S. Hayashi, "Coexistence of two different energy transfer processes in SiO₂ films containing Si nanocrystals and Er", *Journal of Applied Physics*, 95 (2004) 272-280
- [6-2] Albert Polman, Frank C., and J. M. van Veggel, "Broadband sensitizers for erbium-doped planar optical amplifiers: review", *Journal of Optical Society of America B*, 21 (2004) 871-892
-
-

-
- [6-3] F. Priolo, G. Franzo', D. Pacifici, V. Vinciguerra, F. Iacona, and A. Irrera, "Role of the energy transfer in the optical properties of undoped and Er-doped interacting Si nanocrystals", *Journal of Applied Physics*, 89 (2001) 264
- [6-4] A. Polman, "Erbium implanted thin film photonic materials", *Journal of Applied Physics*, 82 (1997) 1-39
- [6-5] Giorgia Franzo, Emanuele Pecora, Francesco Priolo, and Fabio Iacona, "Role of the Si excess on the excitation of Er doped SiO_x", *Applied Physics Letters*, 90 (2007) 183102(1-3)
- [6-6] B. Garrido, C. García, S. -Y. Seo, P. Pellegrino, D. Navarro-Urrios, N. Dalbosso, L. Pavesi, F. Gourbilleau and R. Rizk, "Excitable Er fraction and quenching phenomena in Er-doped SiO₂ layers containing Si nanoclusters", *Physical Review B*, 76 (2007) 245308(1-15)
- [6-7] F. Lenz, R. DeCorby, A. Meldrum, "Sensitization efficiencies in Er-doped SiO_x films containing amorphous or crystalline silicon nanoclusters", *Physica Status Solidi* (2008) A 206, 989-992 (2009)
- [6-8] Oleksandr Savchyn and Pieter G. Kik, Ravi M. Todi and Kevin R. Coffey, "Effect of hydrogen passivation on luminescence-center-mediated Er excitation in Si-rich SiO₂ with and without Si nanocrystals", *Physical Review B*, 77 (2008) 205438 (1-11)
- [6-9] G. Franzò, S. Boninelli, D. Pacifici, F. Priolo, F. Iacona and C. Bongiorno, "Sensitizing properties of amorphous Si clusters on the 1.54- μ m luminescence of Er in Si-rich SiO₂", *Applied Physics Letters*, 82 (2003) 2871-3873
- [6-10] Ji-Hong Jhe, Jung H. Shin, Kyung Joong Kim, and Dae Won Moon, "The characteristic carrier-Er interaction distance in Er-doped a-Si/SiO₂ superlattices formed by ion sputtering", *Applied Physics Letters*, 82 (2003) 4489-4491
- [6-11] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, and K. Yamamoto, "1.54- μ m photoluminescence of Er³⁺ doped into SiO₂ films containing Si nanocrystals: evidence for energy transfer from Si nanocrystals to Er³⁺", *Applied Physics Letters*, 71 (1997) 1198-1200
- [6-12] F. Priolo, G. Franzo', D. Pacifici, V. Vinciguerra, F. Iacona, and A. Irrera, "Role of the energy transfer in the optical properties of undoped and Er-doped interacting Si nanocrystals", *Journal of Applied Physics*, 89 (2001) 264
- [6-13] K. Watanabe, M. Fujii, and S. Hayashi, "Resonant excitation of Er³⁺ by the energy transfer from Si nanocrystals", *Journal of Applied Physics*, 90 (2001) 4761-4767
- [6-14] F. Gourbilleau, M. Levalois, C. Dufour, J. Vicens, and R. Rizk, "Optimized conditions for an enhanced coupling rate between Er ions and Si nanoclusters for an improved 1.54- μ m emission", *Journal of Applied Physics*, 95 (2004) 3717-3722
- [6-15] L. X. Yi, J. Heitmann, R. Scholz and M. Zacharias, "Phase separation of thin SiO layers in amorphous SiO/SiO₂ superlattices during annealing", *Journal of Physics: Condensed Matter*, 15 (2003) S2887-S2895
- [6-16] J. Li, K. Duan, Y. Wang, W. Zhao, Y. Guo, X. Lin, "Modeling and optimizing of high-concentration erbium-doped fiber amplifiers with consideration of ion-clusters", *Optics Communications*, 277 (2007) 143-149
- [6-17] F. Gourbilleau, C. Dufour, M. Levalois, J. Vicens, R. Rizk, C. Sada, F. Enrichi, and G. Battaglin, "Room-temperature 1.54 μ m photoluminescence from Er-doped Si-rich silica layers obtained by reactive magnetron sputtering", *Journal of Applied Physics*, 94 (2003) 3869-3874
- [6-18] Rajni, K. Pita, S. C. Tjin, S. F. Yu, C. H. Kam, "Enhanced photosensitivity in sol-gel derived 20GeO₂:80SiO₂ thin films", *Applied Physics A: Materials Science and Processing*, 82 (2006) 535-541
- [6-19] M. Lopez, B. Garrido, C. Garcia, P. Pellegrino, A. Perez-Rodriguez, J. R. Morante, C. Bonafos, M. Carrada, and A. Claverie, "Elucidation of the surface passivation role on the photoluminescence emission yield of silicon nanocrystals embedded in SiO₂", *Applied Physics Letters*, 80 (2002) 1637-1639
- [6-20] M. L. Bongersma, A. Polman, K.S. Min, E. Boer, T. Tambo, and H. A. Atwater, "Tuning the emission wavelength of Si nanocrystals in SiO₂ by oxidation", *Applied Physics Letters*, 72 (1998) 2577-2579
-

-
- [6-21] G. Allan, C. Delerue, and M. Lannoo, "Electronic Structure of Amorphous Silicon Nanoclusters", *Physical Review Letters*, 78 (1997) 3161-3164
- [7-1] J. Shakya, K. H. Kim, J. Y. Lin, and H. X. Jiang, "Enhanced light extraction in III-nitride ultraviolet photonic crystal light-emitting diodes", *Applied Physics Letters*, 85 (2004) 142-144
- [7-2] M. Boroditsky, T. F. Krauss, R. Coccioli, R. Vrijen, R. Bhat, and E. Yablonovitch, "Light extraction from optically pumped light-emitting diode by thin-slab photonic crystals", *Applied Physics Letters*, 75 (1999) 1036-1038
- [7-3] A. A. Erchak, D. J. Ripin, S. Fan, P. Rakich, J. D. Joannopoulos, E. P. Ippen, G. S. Petrich, and L. A. Kolodziejski, "Enhanced coupling to vertical radiation using a two-dimensional photonic crystal in a semiconductor light-emitting diode", *Applied Physics Letters*, 78 (2001) 563
- [7-4] J. Y. Kim, M. K. Kwon, K. S. Lee, S. J. Park, S. H. Kim, and K. D. Lee, "Enhanced light extraction from GaN-based green light emitting diode with photonic crystal", *Applied Physics Letters*, 91 (2007) 181109
- [7-5] S. H. Kim, K. D. Lee, J. Y. Kim, M. K. Kwon, and S. J. Park, "Fabrication of photonic crystal structures on light emitting diodes by nanoimprint lithography", *Nanotechnology*, 18 (2007) 055306 (1-5)
- [7-6] H. Y. Ryu, Y. H. Lee, R. L. Sellin, and D. Bimberg, "Over 30-fold enhancement of light extraction from free-standing photonic crystal slabs with InGaAs quantum dots at low temperature", *Applied Physics Letters*, 79, 3573-3575 (2001)
- [7-7] J. J. Wierer, M. R. Krames, J. E. Epler, N. F. Gardner, and M. G. Craford, J. R. Wendt and J. A. Simmons, M. M. Sigalas, "InGaN/GaN quantum-well heterostructure light-emitting diodes employing photonic crystal structures", *Applied Physics Letters*, 84 (2004) 3885-3887
- [7-8] S. Fan, P. R. Villeneuve, J. D. Joannopoulos, and E. F. Schubert, "High Extraction Efficiency of Spontaneous Emission from Slabs of Photonic Crystals", *Physical Review Letters*, 78 (1997) 3294-3297
- [7-9] RSOFTE Design manual
- [7-10] S. G. Johnson, S. Fan, P. R. Villeneuve, J. D. Joannopoulos, and L. A. Kolodziejski, "Guided modes in photonic crystal slabs", *Physical Review B*, 60 (1999) 5751-5758
- [7-11] M. Boroditsky, R. Vrijen, T. F. Krauss, R. Coccioli, R. Bhat, and E. Yablonovitch, "Spontaneous emission extraction and Purcell enhancement from thin-film 2-D photonic crystals", *Journal of Lightwave Technology*, 17 (1999) 2096-2112
- [8-1] F. Ay, A. Aydinli, Comparative investigation of hydrogen bonding in silicon based PECVD grown dielectrics for optical waveguides, *Optical Materials*, 26 (2004) 33-46
- [8-2] Daniel P. Poenar, and Reinoud F. Wolffenbuttel, "Thin-film properties of thin-film silicon-compatible materials", *Applied Optics*, 36 (1997) 5122-5128,
- [8-3] R. Germann, H.W.M., Salemin, R. Beyeler, G.L. Bona, F. Horst, I.Masarek, B.J. Offrein, "Silicon oxynitride layers for optical waveguide applications", *Journal of the Electrochemical Society*, 147 6 (2000) 2237-2241
- [8-4] G.L. Bona, R. Germann, B.J. Offrein, "SiON high-refractive index waveguide and planar lightwave circuits", *IBM Journal of Research and Development*, 47 (2003) 239-249.
- [8-5] Ailing Zhang and Kam Tai Chan, "Characterization of the optical loss of an integrated silicon oxynitride optical switch structure", *Applied Physics Letters*, 83 (2003) 2524-2526.
-

Bibliography

- [8-6] R.E. Jones, H.F. Winters, L.I Maissel, Effect of Oxygen on the rf sputtering rate of SiO₂, *Journal of Vacuum Science and Technology*, 5 3 (1967) 84-87
- [8-7] J. B. Lounsbury, Effects of added O₂ upon Argon emission from an rf glow discharge, *Journal of Vacuum Science and Technology*, 6 5 (1969) 838-842
- [8-8] B.S. Sahu , O P Agnihotri, S C Jain, R Mertens and Isamo Kato, “Influence of hydrogen on losses in silicon oxynitride planar optical waveguides”, *Semiconductor Science and Technology*, 15 (2000) L11-L14.
- [8-9] **R.** K. Pandey, L. S. Patil, J. P. Bange, D. R. Patil, A. M. Mahajan, D. S. Patil and D. K. Gautam, “Growth and characterization of SiON thin films by using thermal-CVD machine”, *Optical Materials*, 25 (2004) 1-7