

Fabrication and Characterization of Silicon Rich Oxide (SRO) Thin Film Deposited by Plasma Enhanced CVD for Si Quantum Dot

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Fabrication and Characterization of Silicon Rich Oxide (SRO) Thin Film Deposited by Plasma Enhanced CVD for Si Quantum Dot

By

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Sydney, Australia

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The tandem photovoltaic structure using all Si quantum dots (QD) was proposed and investigated at UNSW. The material with Si quantum dots (QD) embedded in silicate matrices has potential for tunable optical absorption through band-gap engineering.

Si QD materials are generally fabricated by RF-Sputtering followed by high temperature solid-phase crystallization. According to the results of former researchers [9,44], the poor film quality of sputtered films might be responsible for the low conductivity and lifetime of the films hindering the possibility to improve the short circuit current in a Si QD p-i-n structure.

This thesis focuses on ultra thin film silicon rich oxide (SRO) deposition using Microwave-Plasma Enhanced Chemical Vapor Deposition (MW-PECVD), which has the potential of giving higher film quality for intrinsic Hydrogen involvement and less defects after chemical reactions. The electrical properties were not included in this thesis to directly show the advantages of PECVD materials due to the lack of doping gas in MW-PECVD, but the deposition details and the material characterization make the essential way to the electrical property test in future. More advanced doping methods, ion implanting, diffusion source layer or laser assist doping, will be investigated in future.

Another advantage of this technique is its compatibility with large area and high-rate deposition. The parameters related to the deposition rate and the chemical composition were calibrated and will be presented in this thesis.

Thin film superlattice structures were fabricated using a bilayer structure of SRO/SiO2 with 6nm per bilayer. High temperature annealing was carried out for Si QD crystallization. The characterization of chemical properties of SRO was carried out by FT-IR with the support of XPS to identify Si-O, Si-N and Si-H bonds composition before and after annealing. According to the results, the composition of SRO films from PECVD is different from that of the films deposited by RF-Sputtering, especially due to the Nitrogen involvement and the resulting Si crystallization. X-Ray Reflectivity (XRR) was the main approach to determine thin film thickness. X-Ray Diffraction (XRD) and Ramam spectroscopy were applied for the determination of the Si nano-crystal structure. Further improvements for the PECVD thin film deposition and the SRO materials will be discussed. Future work on the utilization of other characterization techniques and the doping of SRO and Si QD will also be discussed.

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Abstract

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Contents

ABSTRAC	Т	II
ACKNOWI	_EDGEMENT	IV
CONTENT	S	5
CHAPTER	1. INTRODUCTION	7
1.1. THE	Motivation	7
1.2. EFFI	CIENCY LIMIT ANALYSIS	
1.3. TAN	DEM SOLAR CELL USING ALL SI QUANTUM DOT (QD)	10
1.4. THE	SIS STRUCTURE	12
CHAPTER	2. LITERATURE REVIEW	13
2.1. RES	EARCH ON SI QUANTUM DOTS AND QD DEVICE	13
2.2. SILIC	CON RICH OXIDE BY PECVD	17
2.3. PUL	SE PECVD DEPOSITION FOR SRO	
CHAPTER	3 FABRICATION AND CHARACTERIZATION METHODS	23
3.1. PLA		
3.1.1. 3.1.2	Principles of PECVD Deposition	23
3.1.3.	The Parameters in PECVD Deposition	
3.1.3	3.1. Substrate Temperature	
3.1.3	3.2. Flow Ratio/ Rate	
3.1.3	3.4. Pressure	
3.1.4.	PECVD Configurations	30
3.1.4	4.1. Remote-PECVD	
3.2. Сна	RACTERIZATION TECHNIQUES FOR SRO	
3.2.1.	Fourier Transfer Infrared Spectroscopy (FTIR)	
3.2.1	1.1. FT-IR Introduction	37
3.2.1 3.2.1	1.2. Absorption Spectroscopy of SRO 1.3. Data Processing and Sample Requirements	
3.2.2.	X-ray Photoelectron Spectroscopy (XPS)	
3.2.3.	Raman Spectroscopy	
3.2.4.	X-ray Diffraction (XRD)	
3.2.5.	X-ray Reflectivity (XRR)	47
3.2.6.	Photoluminescence	49
CHAPTER	4. EXPERIMENT & DISCUSSION	52
4.1. MON	IOLAYER SRO DEPOSITION	52
4.1.1.	Substrate Temperature	52
4.1.2.	MW Plasma Power	54

4.1.3.	Argon Flow Rate Influence	56
4.1.4.	SiH₄ Flow Rate to Deposition Rate	58
4.1.5.	SiH ₄ /N ₂ O Ratio to Composition	59
4.1.6.	Uniformity Improvement	61
4.2. SUP	ERLATTICE DEPOSITION	61
4.2.1.	Pulse Deposition Method for Thin Film Deposition	61
4.2.2.	FTIR & XPS for Pulse Deposition	63
4.2.3.	SiO2/SRO Superlattice by Pulse Deposition	65
4.3. Ann	EALING OF SRO THIN FILM	67
4.3.1.	SRO Compositional Change by Annealing	67
4.3.2.	XRD & Raman Analysis on Si Crystallization	68
CHAPTER	5. CONCLUSIONS & FUTURE WORK	72
CHAPTER 5.1. MW·	5. CONCLUSIONS & FUTURE WORK	72 72
CHAPTER 5.1. MW- 5.1.1.	5. CONCLUSIONS & FUTURE WORK -PECVD FOR THIN FILM DEPOSITION Deposition Rate	72 72 72
CHAPTER 5.1. MW- 5.1.1. 5.1.2.	5. CONCLUSIONS & FUTURE WORK PECVD FOR THIN FILM DEPOSITION Deposition Rate Chemical Properties of SRO	
CHAPTER 5.1. MW- 5.1.1. 5.1.2. 5.1.3.	5. CONCLUSIONS & FUTURE WORK PECVD FOR THIN FILM DEPOSITION Deposition Rate Chemical Properties of SRO Fabrication Improvement	72 72 72 72 72 73
CHAPTER 5.1. MW 5.1.1. 5.1.2. 5.1.3. 5.2. THE	5. CONCLUSIONS & FUTURE WORK -PECVD FOR THIN FILM DEPOSITION Deposition Rate Chemical Properties of SRO Fabrication Improvement SILICON RICH OXIDE (SRO) FOR SI QD	72 72 72 72 73 74
CHAPTER 5.1. MW 5.1.1. 5.1.2. 5.1.3. 5.2. THE 5.3. FUTU	5. CONCLUSIONS & FUTURE WORK PECVD FOR THIN FILM DEPOSITION Deposition Rate Chemical Properties of SRO Fabrication Improvement SILICON RICH OXIDE (SRO) FOR SI QD JRE WORK FOR SRO AND SI QD	72 72 72 72 73 74 75
CHAPTER 5.1. MW- 5.1.1. 5.1.2. 5.1.3. 5.2. THE 5.3. FUTU 5.3.1.	5. CONCLUSIONS & FUTURE WORK PECVD FOR THIN FILM DEPOSITION Deposition Rate Chemical Properties of SRO Fabrication Improvement SILICON RICH OXIDE (SRO) FOR SI QD JRE WORK FOR SRO AND SI QD Characterization	72 72 72 73 74 75 75
CHAPTER 5.1. MW- 5.1.1. 5.1.2. 5.1.3. 5.2. THE 5.3. FUTU 5.3.1. 5.3.2.	5. CONCLUSIONS & FUTURE WORK -PECVD FOR THIN FILM DEPOSITION Deposition Rate Chemical Properties of SRO Fabrication Improvement SILICON RICH OXIDE (SRO) FOR SI QD JRE WORK FOR SRO AND SI QD Characterization Device Fabrication	72 72 72 72 73 74 75 76

Chapter 1. Introduction

1.1. The Motivation

People around the world are accepting the photovoltaic technology as the up and coming energy-harvesting method of choice. Utility products like solar farms, roof solar systems and remote area electricity solutions are changing people's lives. From a researcher's point of view, there is still a large parameter space to improve photovoltaic technology in order to support better energy conversion products. The manufacturing cost will be cut, III-V/II-VI semiconductor [3,7], organic [6] and even nano materials [14,30,47] will be applied, and new solar cell structures will appear to improve conversion efficiency and product appearance.

One of the most fundamental key points in solar cell research is the energy conversion efficiency improvement. For this purpose, Si quantum dots (QD) [52] have the potential to open the way to new solar cell structures that will break the efficiency limit.

In UNSW, RF-Sputtering is generally used to fabricate SRO materials. After high temperature solid-phase crystallization, amorphous Si crystallizes to Si QD. However, the poor film quality of sputtered films (defects formed in physical reaction) might be responsible for the low conductivity and lifetime of the films hindering the possibility to improve the short circuit current in a Si QD p-i-n structure [9,44].

This thesis aims to contribute efforts in the field of Si Quantum Dot (QD) by reporting on the fabrication and characterization of Silicon Rich Oxide (SRO) thin films deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD). It is expected the films deposited by chemical reaction contains less dangling bonds, especially at the interface of Si QD [15].

The literature review included in this Master's research thesis aims to summarize the necessary knowledge of PECVD deposition and characterization techniques for thin film materials. This literature review aims to be used as a reference and record for researchers who want to continue working on the fabrication of superlattice structures by PECVD. Besides the

literature review on the general principles, specific applications of PECVD and characterization techniques on SRO thin film materials are included.

Another main objective of this Master's project is the fabrication of thin film SiO₂ and SRO materials in a superlattice structure using MW-PECVD. This is the first necessary step to produce Si QD films and devices using MW-PECVD SRO layers. Although more work is still needed on the optimization of the deposition parameters, it has been demonstrated that it is possible to use MW-PECVD to deposit SiO₂/SRO thin films and superlattice structures. The different characterization techniques reported here give us a clearer understanding of some of the chemical and physical characteristics of MW-PECVD SRO films.

1.2. Efficiency Limit Analysis

In theory, solar cells based on semiconductor materials (Si, Ge or GaAs etc.) using a single p-n junction structure could reach a maximum efficiency of 32%, which is known as Shockley & Queisser efficiency limit [50]. In the laboratory, the highest 25% efficient world record is held by a PERL (Passivated Emitter Rear Locally diffused) Si solar cell structure developed at UNSW [56]. In industry, using bulk Si wafers it is possible in highly commercialized solar cells to reach the efficiency around 20%

Meanwhile, the thin film solar cell, which is only 2-10um thick, has been investigated for decades involving more semiconductor processing technologies such as CVD, MBE, lithography and Reactive Ion Etching (RIE) etc. Typical a-Si single junction solar cell can reach around 10%. The micromorph cell [26], a-Si:H/u-Si:H double-junction cell, has a stabilized efficiency of 12.5% and is commercially produced [42,25].

Other types of solar cells such as CIGS [41,54], CdTe [7], dye-sensitized [40] or organic solar cells all have good efficiency and low cost advantages. However, single junction cell or solar cells using single absorber material has not reached the SQ efficiency limit of 32%.

Astonishingly, the III-V tandem structure solar cell has reached 34% under one sun and even over 43% efficiency under concentrated solar radiation [21].

The main reason for the high efficiency is the tandem structure using materials with different band gaps that reduces thermailisation losses by more optimally absorbing the solar spectrum.

The idea of tandem structure derives from the analysis of the energy loss in semiconductor p-n junction. In figure 1, it shows the five possible losses in a single junction device based on the band structure theory.



Figure 1. Illustration of the energy loss mechanisms in single junction semiconductor solar cell [10].

Photon energy lower than the material's bandgap will pass through the material without absorption (1). On the other hand, the photons with excessive energy over the bandgap will generate electron-hole pairs. The excess energy will be wasted as heat when electrons or holes thermalise to the band edges (2). The sub-bandgap photon loss mechanism (1) and the thermalisation effect (2) are responsible for a very serious loss of efficiency, contributing 23% and 33% loss of the solar radiation power respectively [44].

Additionally, the carriers will lose energy while traveling across the junction and contact, which are the loss mechanisms (3) and (4). As the last loss mechanic, the recombination (5) is an inevitable loss for any semiconductor, which is generally quantified by lifetime of minority carriers. In the case of Shockley and Queisser's efficiency calculation, the recombination occurs entirely as radiative which is the main recombination mechanism that cannot be avoided, even in a perfect semiconductor. If Auger (also unavoidable), trap assisted and surface recombination mechanisms are considered, which are more possible recombination mechanics in practice, it will cause the maximum attainable efficiency to be lower. One of the most immediate ways to overcome the Shockley and Queisser's efficiency is to use materials with higher to lower bandgaps stacked on top of each other to harvest over 50% of the energy that is lost due to hot carriers relaxation and non-absorbed photons. Following Shockley and Queisser's assumptions for the multi-junction PV structure, the double-junction cell can reach as high as 42.8% efficiency by choosing band gaps as 0.98eV and 1.87eV. The tripe junction solar cell theoretically can achieve the 47.3% efficiency [19,44].

1.3. Tandem Solar Cell Using All Si Quantum Dot (QD)

The highest efficiency tandem solar cells are fabricated using III-V group elements in the structure of GaInP(1.88)/GaAs/GaInAs(0.97) [1]. Epitaxial deposition techniques like MBE are essential to attain lattice matching at the film interfaces, which constrains the selection choices of materials. By using buffering layers, lattice mismatched materials can be stacked together with very low defect concentration at interfaces [53]. But the complexity of epitaxial deposition, high equipment requirement and rare semiconductor materials limit the fabrication of these cells at an industrial scale. The extremely high cost makes these solar cell devices mainly attractive to space or military applications.

Al
n-GaAs contact
n-AlInP window
n-InGaP emitter
P-InGaP base
p-AlInP BSF
p-AlGaAs/n-InGaP
n-InGaP window
n-InGaAs emitter
p-InGaAs base
p-InGaP BSF
p-AlGaAs/n-InGaP
n-InGaAs buffer
InGaP 1 st layer
n-Ge
p-Ge
Al

Figure 2. Schematic illustration of one triple junction solar cell structure.

A very important requirement for the tandem structure PV devices (Figure.2) is the materials having various bandgaps values. Therefore, the Quantum Dot (QD) materials [52], enabling the researchers to design the materials'

bandgap, could make these materials amenable for tandem solar cells. The term "quantum dots" refers to semiconductor clusters in nanometer size embedded in the material with a higher bandgap. In such a structure, the behaviour of the electrons differs from that of the bulk semiconductor.

In a simple quantum well model, the electrons confined in potential wells will form discrete effective energy levels so that an effective wider optical band gap forms and depends on well dimension and potential energy differences between the dot material and the matrix. Si clusters of a few nanometers in size or nc-Si embedded in SiO_2 , SiN_x and SiC can be modeled as a three dimensional (3D) quantum well. Compared to the 1D quantum well, it would have stronger confinement so as to attain a higher effective band gap. Therefore, Si bandgap engineering is possible if the Si QD dimension and its microstructure can be controlled.



Figure 3. The schematic structure of tandem PV device using Si QDs. [9]

Based on the quantum effects in nc-Si, an all-Si quantum dot solar cell was proposed as shown in Figure.3 [20]. Si quantum dot materials have been investigated in UNSW for a long time. In general, SiO_2 , SiN_x and SiC have been used as the matrix. Si nano-crystals are formed by segregating excess Si into Si QDs after high temperature annealing.

1.4. Thesis Structure

The aim in this thesis is to investigate the structural, chemical and optical properties of Silicon Rich Oxide fabricated by Microwave-PECVD for nc-Si QD formation as the fundamental material used for Si QD PV device.

In Chapter 2, the literature review focuses on the research of Si quantum dot solar cell devices and the silicon rich oxides material.

In Chapter 3, the PECVD deposition and the characterization techniques used in this thesis will be reviewed in details. The principles of various Plasma enhanced CVD depositions are described. The parameters in PECVD controlling SiO₂ and SRO thin film quality are included. For the chemical and structural properties, the review of the principles and applications of the characterization techniques, including Fourier Transform Infrared Spectroscopy (FTIR), XPS, XRD/XRR, Raman spectroscopy are discussed

Chapter 4 reports experiments on thin film SRO and SRO/SiO₂ superlattice preparation using PECVD and the discussion according to the characterization results on these materials. The PECVD parameters were calibrated for the thin film deposition rate, composition and formation of superlatice structures. Steady state and the pulse deposition methods are compared. Annealing and its effect on chemical and structural changes will be presented.

Chapter 5 is the conclusion of the thesis. It also includes the discussions on the PECVD deposition of SRO and further proposed improvements for future work.

Chapter 2. Literature review

2.1. Research on Si Quantum Dots and QD Device

The density and the size of the Si quantum dots formed in dielectric materials are significant factors for the quantum confinement and mini-band formation among the Si QDs. In order to better control the QD size, superlattice structures of SiO₂/SRO have shown to be an effective method to constrain Si crystal growth in SRO layers [18]. At UNSW, an AJA RF-magnetron sputtering machine has been used to deposit thin film silicon rich dielectric materials [14]. The deposition rate can be control with rates as low as 2-3nm/min for SiO₂ and 1-2nm/min for a-Si so accurate control on the thickness is possible. Si, SiO₂, SiN_x and SiC targets are commonly used. The Si richness can be adjusted by controlling the amount of materials deposited by using shutters and varying the sputtering power during the deposition. Annealing is essential for Si crystals formation. Typically, the time for annealing varies for different annealing methods. High temperature furnace annealing at 1100°C in N₂ atmosphere takes approximately 1 hour and less than 10minutes for Rapid Thermal Annealing (RTA) [13,36].

In High definition TEM images (Figure.4), it is easy to see the SiO_2/SRO superlattice structure. The area showing fringes represents Si atoms in crystalline form. These crystals have random orientations and are distribute in SiO_2 . In these TEM images, the Si QD can be found to be in the range of 2-4 nm in diameter.



Figure 4. nc-Si formed in SiO_{1.3}/SiO₂ structure after 1100°C annealing [22].



Figure 5. PL peak shifts to higher energy for nc-Si size decreases. However, the red shift for nc-Si size from 4-5nm indicates other PL mechanisms other than quantum confinement.

The Photoluminescence (PL) peak shift effect is commonly regarded as an evidence of effective bandgap engineering due to quantum confinement. By controlling the Si size, PL peaks shift according to expectation that smaller Si QD size will have lower wavelength PL emission. As shown in Figure.5, Si QD in 1.8nm size shows PL peak around 1.65V, which is 0.2eV larger than Si QD size around 4-5nm. By looking into the details of the optical emission

properties by transient PL results, different emission mechanisms will be revealed [12].

The first attempt on diode device fabrication was carried out at UNSW by solely using Si quantum dot materials on quartz substrates [46]. The p-n structure (Figure.6) consists of 25 SiO₂/SRO bilayers with very high Boron concentration, 10 SiO₂/SRO bilayers with no doping and 35 SiO₂/SRO bilayers with Phosphorus doping. After annealing, inter-diffusion forms a p-n structure rather than the intended pin structure. In each bilayer, there are 2nm SiO2 and 4nm SRO. The doping sources used were metal B and P2O5 targets used for in-situ doping of SRO layers. Using quartz substrate instead of Si substrates, eliminates the possibility of a junction formed between the QD material and the substrate.



Figure 6. The p-i-n structre was fabricated with B/P doping. SiO2/SRO (2nm/4nm) superlattice structure is shown. The AI back contact was fabricated, which induce large sheet resistivity [46].



Figure 7. Rectifying I-V curve can be found in the p-i-n structure. The Voc was 373mV in the graph and was improved to 490mV [46].

Using this structure, a rectifying diode behavior was achieved (Figure.7). The open circuit voltage was optimized to reach 490 mV. Due to the extremely high sheet resistivity of SRO/SiO₂, very small currents could be extracted. Although doping has been achieved by adding large amounts of B/P in SiO₂/SRO materials, it seems the doping is not very effective as the sheet resistivity is higher than 1×10^6 ohms per square [36]. This high resistivity posed a big problem for a back contact metallization scheme. One explanation for the high resistivity is the low tunneling current, which might be improved by using SiN_x barrier layers rather than SiO₂ [13]. However SiN_x exhibits less quantum confinement. So far it seems SiN_x/SRO superlattices have a reasonable chance to improve the current and still maintain Si QD formation.

There is still large space for the investigation on the doping of quantum dots by determining the conductivity, quantum dot formation and junction. Applying other thin film deposition techniques will give different properties to the SRO, which might improve the ultimate device performance.

2.2. Silicon Rich Oxide by PECVD

For Silicon rich oxide deposition by PECVD, the silicon sources are usually SiH₄ and TEOS (Tetra-Ethoxy-Silane: Si(OC₂H₅)₄) and the Oxygen sources are usually O₂, O₃, N₂O and CO₂. Unlike SiH₄, which is in gas form at room temperature, the TEOS is in liquid form, so for the PECVD reactions an inert carrier gas (like N₂) is necessary. In TEOS, the silicon atom is already oxidized so it is easier to convert to SiO2 at high temperature. Usually, people use TEOS is used with O₂ for SiO₂ deposition or as well as SiH₄ combined with O₂, N₂O and CO₂. TEOS/O₂ is usually used for SiO₂ deposition in PECVD but not in LPCVD due to the moisture formation resulting from large amount of H and O. It is also known that TEOS/O₂ by PECVD has a better conformal deposition than Silane/O₂ PECVD or thermal deposition [37]. But it is rare to use TEOS/O₂ to deposit silicon rich oxide because the already formed Si-O bonds in TEOS, which might be due to the Si-O in TEOS. Therefore, the silane is still the most popular gas for silicon rich oxide thin film deposition.

Using different Oxygen sources (O₂, N₂O, CO₂) will change the silicon rich oxide properties. The easiest way to get pure SiO₂ is to use O₂ with SiH₄. By changing the SiH_4/O_2 flow ratio, it is immediately possible to change the stoichiometry. However, it was found that the moisture formed by large H and O content is a serious problem. Additionally, the O_2 is chemically too reactive to form particles and increases the difficulty to control the reaction. It is rare to see researchers to use Silane/O₂ in RF-PECVD for SiO₂ deposition. The application of Remote-PECVD using Silane/O₂ makes it possible to achieve SiO₂ films with higher quality than those obtained from the usual Remote-PECVD using SiH₄ and N₂O. The quality of the Silane/O₂ films is comparable to that of thermal oxides (Figure 8). In Figure 8, the defect density of SiO_2 by PECVD is comparable with the thermal SiO₂. In Silane/O₂ Remote PECVD, an ICP plasma source is used on top of the chamber to excite O₂ and He flowing downwards. The showerhead used for the SiH₄ inlet is located around the substrate underneath and outside the plasma region. The deposition rate can be slowed down significantly and 1-2nm/min is achievable. By changing the N₂O/SiH₄ ratio, it is possible to achieve silicon rich oxide (SiO_x) with x=1 [5].



Figure 8. The remote-PECVD in RWTH Aachen University is able to achieve SiO2 films with very low defect density [24].

As an alternative, N₂O is more widely used for SiO₂ PECVD deposition. It can be used equally well in RF-PECVD and Remote-PECVD for SiO₂ films with good isolation quality. It overcomes the disadvantages of O₂ that the film from N₂O has lower chemical reactivity and less moisture problems. More importantly, by using N₂O it is possible to create any stoichiometry, from pure a-Si to stoichiometric silicon dioxide by varying the mixture of SiH₄ and N₂O. In this combination of gases, the plasma excites the N₂O to dissociate into N₂ and O ions (O^{*} or O_2^*) then the O ions or excited precursors will further react with SiH₄ to generate $SiO_xH_v^*$ precursors then to form SiO₂. Kushner proposed that SiH₃O and SiH₂O [28] were essential for producing SiO₂ and Longway et al. reveal that is (SiH₃)₂O what is actually needed [33]. However, the SiH₄ dissociation is a very complicated process as there are many different precursors to open up many reaction paths in the plasma. Therefore, the identification of the precursors is still under debate. Direct plasma excitation and remote plasma excitation will definitely generate different SiH₄ precursors and, as a result, the SiO₂ films formed will have different properties such as various H or N content and stoichiometry. Generally, Direct-PECVD

will produce non-stoichiometric SiO_x films with larger bonded hydrogen content. But Remote-PECVD is able to deposit stoichiometric SiO_2 with less H [34].

The basic dissociation reactions in SiH₄/N₂O are as follows [17,55]:

Due to the Nitrogen atoms in N_2O , it is conceivable that the N will be inevitably involved in the film (Figure.9). This indeed might be the case because of the excited NO to form N-H and Si-N bonds. It is found that the Si content increase with the increasing SiH₄/N₂O ratio but the N content would also increase up to 20 at% in RF-PECVD (Figure.9). The problem is that the O content decreases with increasing SiH₄. It is not clear why the oxygen content decreases.

There are few reports about using CO_2 for PECVD SiO_2 deposition. The energy for CO_2 CVD deposition is much larger than using O_2 or N_2O . But in PECVD, it is possible to use CO_2 to produce SiO_2 [4]. For Silicon rich oxide films, it is straightforward to change the SiH₄/CO₂ ratio to adjust the silicon richness. It is also found that C at% incorporated in SiO_x film is only around 2 at% so its impact on the SiO_x film properties is minimal [11].



Figure 9. Increasing SiH_4/N_2O ratio increase the N content and Si content, meanwhile the O content decreases [2].

2.3. Pulse PECVD deposition for SRO

In industry, PECVD produces high quality thin film semiconductor materials. It is also high rate deposition technique. For the research purposes in laboratory, especially for films in nanometer thickness, ultra low film deposition rate is necessary.

Plasma source is the most significant aspect for deposition rate because it will determine whether it is direct or remote plasma in deposition. The remote plasma has much lower deposition rate than direct plasma [34]. Inductively coupled plasma source or microwave plasmas source is usually used to build remote plasma. Moreover, the requirement of vacuum system is relatively lower. The deposition rate can be controlled as low as 1nm/min if necessary [24] (Figure.24).

The compromise for making thin film deposition by general PECVD is to use pulse power source to ignite plasma. By controlling plasma power in very short time, as in 2-20s, ultra thin film can be achieved. By applying pulse RF power generator in RF-PECVD (Figure.10), ultra low deposition rate lower than 2 A/cycle is possible to deposit ZnO [57].



Figure 10. Pulse RF-PECVD for ultra thin film deposition.

Besides controlling pulse time as 2-20s, the purging reactants and byproducts before and after plasma ignition are also critical to ensure the consistency of deposition conditions for each layer.

Although the pulse deposition is able to achieve the ultra thin films, there are inevitable disadvantages must be considered:

- Deposition rate is not constant during the pulse because the plasma takes time to become stable. Therefore, the unit nm/cycle should be used rather than nm/min or A/s. As a result, it takes time to calibrate the right pulse and purging time.
- The film composition by pulse deposition could be different from those by stable deposition. If pulse time is too long, there might be gradient property from bottom to top in each layer.
- Another issue could happen is the byproducts in plasma absorbed by the chamber would be desorbed back into the plasma. Therefore longer purging time helps but makes the deposition time longer.

As our goal is to fabricate SRO/SiO2 superlattice, the drawback of nonuniform film is not detrimental as long as we make the thickness thin enough, like 3-5nm. So it should be still feasible to control the Si quantum dot size by controlling SRO thickness after 1100C annealing.

Chapter 3. Fabrication and Characterization Methods

3.1. Plasma Enhanced Chemical Vapor Deposition (PECVD)

3.1.1. Introduction of Thin Film Deposition

Thin film deposition technique include physical vapor deposition (PVD) and chemical vapor deposition (CVD) [38].

Physical Vapor Deposition (PVD)

Chemical Vapor Deposition (CVD)

• Sputtering

LPCVD (Low Pressure CVD)

- Evaporation
- E-Beam evaporation
- APCVD (Atmosphere Pressure CVD)
- PECVD (Plasma Enhanced CVD)
- LACVD (Laser Assisted CVD)
- HWCVD (Hot Wire CVD)
- MOCVD (Metalorganic CVD)

The PVD deposition reaction starts from the evaporation of solid phase or liquid phase material into gas phase, then the gas phase atoms and molecules move through high vacuum or low-pressure gaseous plasma to the substrate and condense into solid thin film [39]. The evaporation of target materials can be achieved in vacuum condition by high temperature heating, inert gas plasma bombardment or electron beam bombardment. The advantage of PVD is that almost any solid phase inorganic material can be deposited. The deposition rate is relatively low ranging from 1 to 100 Å/Second. In regards to the thin film quality, more voids and defects usually appear compared to Chemical Vapor Deposition (CVD). It is rare to get epitaxial growth by PVD unless using very high substrate temperature.

In Chemical Vapor Deposition (CVD), the chemical reactions start from a gasphase reaction on the substrate surface to then form the solid-phase films. In CVD, gas phase reactants move to the substrate, near the surface reaction region. The high surface temperature (from 900°C to 1100°C) on the substrate will thermally activate the reactants adsorbed on the surface of substrate to start chemical reactions [38]. Meanwhile, the reaction byproducts are desorbed in gas phase. By controlling the temperature and gas flow rate, determining both the reactants transport rate and the surface chemical reaction rate, it is able to control the deposition rate. This technique also makes it possible to obtain epitaxially grown films.

In LPCVD using low pressure and high temperature, it is possible to achieve very high film quality with fewer voids, fewer defects and higher density [38]. The disadvantages of thermal CVD are the very low deposition rate and the large thermal consumption, so these limit its use for mass production in industry. More significantly, the use of high substrate temperature limits the selection of substrates or the possibility of deposition on the volatile films in high temperature.



Figure 11. Plasma Enhanced CVD using capacitively coupled RF-plasma generator [48].

The application of plasma is able to dramatically improve the CVD techniques to overcome the disadvantages of thermal CVD. The plasma contains partially ionized and excited gas precursors in the high vacuum condition. Typically a 13.56MHz Radio-Frequency power source is used to sustain the plasma in between two steel capacitive plates. As the reactants have been partially activated in plasma, thermal activation is not necessary. Therefore Plasma Enhanced CVD (PECVD) is able to reduce the substrate temperature to 200°C-400°C. This technique also improves the deposition rate by 2-5 times larger compared to thermal CVD such as LPCVD. More importantly, various gas precursors can be used to deposit thin film materials including dielectrics, metals and polymers. As the reaction is generally maintained in a vacuum

condition, the high quality thin films with low impurity concentrations can be achieved. The disadvantage of this technique is that it introduces relatively more chemical and particulate impurities compared to LPCVD.

By using plasma, the substrate and films will suffer ion bombardment due to the intrinsic DC bias formed between the plasma and the substrate (Figure.11). The ion bombardment could degrade the film quality and increase surface roughness. In despite, by controlling the ion bombardment, the film stress can be controlled as high bombardment will produce denser films with compressive stress and low bombardment will induce tensile stress. The films deposited by PECVD can be very different by changing parameters such as substrate temperature, inert gas ratio, surface modification and different plasma sources. Therefore PECVD has become a very versatile thin film deposition tool.

In industry, PECVD has become the most widely used and well-developed technique for large area thin film deposition. Its high uniformity performance, low substrate temperature and high deposition rate enable the manufacturers to fabricate devices in scales from nanometers to meters. For example, from MEMS sensor to flat panel LCD/LED TV and thin film solar cells. In solar cell manufacture, PECVD is an indispensable tool to obtain high quality and stable Si₃N₄ passivation and anti-reflection coating. Al₂O₃ rear passivation is also commercially achieved by PECVD.

3.1.2. Principles of PECVD Deposition

The plasma is defined as the gas in quasi-neutral state ($n_e=n_i$) consisting of positive ions/excited species and highly energized negative electrons. In PECVD, the plasma is usually generated by delivering energy to the gas precursors by Radio Frequency or microwave power supply in a vacuum condition. The electrons have much smaller mass than atoms or molecules so that an external RF electric field or microwave can easily accelerate the electrons to give them very high kinetic energy. When the electrons are being accelerated, collision between electrons and molecules will occur so the electron can break atoms or molecules to generate reactive ions, radicals and excited atoms or molecules. Meanwhile, the recombination of electrons and

ions will happen spontaneously to emit lights, which is the reason for the characteristic glow emitted by a plasma. However, the ionization fraction is very small. For instance, in the capacitively coupled plasma, the ionization fraction only reaches 10⁻⁵ [31]. Therefore, much energy will be lost in particle collision, recombination and ion bombardment, but less heat will be generated.

In PECVD, the plasma is a cold plasma because the real temperature is not high, which is only slightly higher than the substrate temperature near the substrate surface. However, the electron temperature is extremely high. It can reach as high as 1-10eV (1eV=11605K) for capacitively coupled plasma at the pressure of 1-1000 mTorr [32]. In cold plasma, the ion temperature is much lower than the electron temperature ($T_i << T_e$), so the plasma in PECVD is not in equilibrium condition. These positive ions or excited molecules do not function to deliver heat to the substrate, but they are very physically or chemically reactive on the surface adsorption sites.



Figure 12. Plasma helps to increase the reactant gas chemical and product chemical potential so less energy is required to start the reaction [48]. ΔE^* is the chemical potential required in plasma and it is less than ΔE in the normal gas reaction.

The activation of gas precursors in plasma dramatically increases the chemical potential of reactants so that the low temperature heating or light energy is enough to start the chemical reaction (Figure.12). That is why PECVD can deposit thin films at very low substrate temperature even at room temperature [27].

3.1.3. The Parameters in PECVD Deposition

Controlling the plasma is a complicated matter for film deposition compared to evaporation and sputtering. The basic requirement for thin film deposition technique is to control the deposition rate, film composition, even doping, refractive index and micro- or nano-structure. Therefore, this part will review the parameters in PECVD for film deposition control.

3.1.3.1. Substrate Temperature

Although the use of plasma makes the CVD possible to deposit films at room temperature, the substrate temperature between 200 °C to 400 °C is still necessary for the chemical reaction and to achieve better film quality. Generally, the higher substrate temperature improves the film uniformity, and produces less voids and stronger bonds. The reason for this is that the ions and precursors adsorbed on the substrate surface will have the mobility to move around the surface to find the site for stronger bonding. The higher substrate temperature means higher mobility of the adsorbed ions/precursors so that the ions/precursors are able to find the stronger bond sites before being covered by other arriving ions/precursors. Also as a result, less voids and defects will form. This is also one significant reason why the PVD or CVD at higher substrate temperature can produce epitaxial thin film.

Actually, the substrate temperature has very slight influence on the deposition rate because the real temperature determining the chemical reaction is the electron and the ion temperature, which are considerably larger than the substrate temperature. However, from the author's experience, rising temperature will slightly increase deposition rate in Direct-PECVD used in CCP configuration. It might be because the thermal activation at high temperature slightly enhances the surface chemical reaction rate at the low plasma density. In the case of high plasma density, ion adsorption and bombardment dominates the chemical reaction, and a high substrate temperature has even less effect on the deposition rate.

The weak bonds are broken by high thermal processing and also by ion bombardment. This is one issue to consider when high temperatures over 400° C when SiH₄ is in use because higher temperature tends to break Si-H and release H₂. Generally, 480°C annealing is used for dehydrogenation in a-Si since the Si-H bond starts to break at this temperature. If the high

temperature is applied in PECVD deposition, H content will drop compared to the deposition at lower substrate temperature.

3.1.3.2. Flow Ratio/ Rate

In terms of dielectric thin film deposition by PECVD, such as SiO_2 and Si_3N_4 , adjusting the reaction gas ratio is generally a way to control the stoichiometry. For SiO₂ deposition, SiH₄ and N₂O are the gases usually used in PECVD. In order to get stoichiometric SiO₂, over flowing N₂O gas (High N₂O: SiH₄ ratio) to oxidize SiH₄ is usually applied. Also it is straightforward to increase the Si content by increasing SiH₄/N₂O ratio. But the involvement of Nitrogen content becomes an issue when SiH₄/N₂O ratio increases. It was reported that the O content will decrease and N and Si content will increase when the SiH₄/N₂O ratio increases in RF-PECVD. When the ratio reaches that SiH₄: N₂O=1, the content of Si and O become almost equal and further increasing SiH4 flow will make the film Nitrogen rich and the content of Nitrogen will be comparable to O content [2]. Generally, the Nitrogen content will not exceed 20 at% in films fabricated by RF-PECVD using CCP. Similarly, C content increases when SiH_4/CO_2 ratio increases. Therefore using O_2 for reaction will eliminate the impurity involvement. However, due to the high chemical reactivity of O₂, the reaction becomes very intensive and the gas-phase reaction will form SiO₂ or a-Si powders in PECVD. As a result, a low deposition pressure is necessary for O₂. Usually, SiH₄ and O₂ can be used in remote PECVD where low deposition and low pressure are used.

The gas flow rate determines the residence time of reactants in the chamber. Higher flow rate reduces the residence time so as to increase the reactant concentration in the chamber. In RF-PECVD, it is a minor influence on the deposition rate because the deposition is reaction-limited process rather than a transport-limited process. The RF-PECVD chamber used for research purpose is generally designed in 'differential' condition so that the precursor concentrations at the gas inlet and that at the gas outlet are almost the same, and only a small amount of gases in the chamber will be involved in the reaction. As a result, the rate is more related to the plasma density, pressure and bias voltage as these determine the reaction rate. The situation will be different in remote-PECVD where the reaction depends more on the availability of reactants since the SiH_4 is not directly excited and the substrate is placed outside the plasma region. So it is more dependent on the availability of SiH_4 .

3.1.3.3. Power Supply and Power Frequency

There is a proportional relationship between the RF plasma power and the deposition rate in RF-PECVD. Higher RF plasma power generates denser plasma, which means a higher ionization and excitation fraction. As the deposition rate depends on the concentration of ions and excited precursors, the overall deposition rate increases.

Another aspect that should be considered is the ion bombardment, which increase with plasma density and induces more surface states and defects in films. For RF-PECVD in CCP configuration, the ion bombardment energy E_i can reach $V_{rf}/2$ eV, even as high as V_{rf} eV if the electrode area is reduced [31]. It is an advantage if an ion etching process is desired but can become be a problem since the ion bombardment energy and ion-bombarding flux cannot be separately controlled. In RF-PECVD, lower power is always preferred for deposition.

The power frequency has a direct effect on the film quality because the frequency determines the electron temperature that determines the ionization and ion bombardment. Higher RF frequency power can generate highly confined plasma that will have a lower ion bombardment effect on the substrate surface. The electrons in high frequency plasma have higher electron temperature and are more efficient at ionizing the gas precursors. So deposition rate is improved due to higher plasma density. The films usually have lower density and tensile stress.

On the contrary, low RF frequency power is able to accelerate the ions for a longer time to give the ions higher kinetic energy. So more ions tend to arrive at the surface and bombard the substrate. As a result, there will be higher density and compressive stress in the film.

In industry, it is usual to install two power supplies with high and low frequencies on the electrodes respectively in RF-PECVD. The High frequency is used to control the plasma density and low frequency is for ion bombardment control. It is then possible to control the film stress by controlling the power ratio between the two power supplies.

3.1.3.4. Pressure

The pressure mainly determines the reactant gas concentration, precursor residence time and mean free path of the electrons in the chamber. Therefore it directly determines the deposition rate. The normal deposition pressure ranges from1 mTorr to 1000 mTorr for PECVD. When the pressure increases the deposition rate increases but the uniformity will suffer. In order to achieve thin films with high uniformity, the low pressure is necessary. Because the lower pressure means the higher diffusivity (D) thus at constant surface temperature the mass transport is enough for surface reactions to occur. The uniformity is improved by a more uniform concentration on the surface in a low-pressure atmosphere.

However, if the pressure goes too low it becomes difficult to generate a stable plasma. This is because the mean free path of electrons at low pressure is long so as to cause fewer electrons to collide with molecules effectively before they hit the walls. So it is helpful to find the right pressure values first according to the requirements for the required deposition rate, then to adjust other parameters.

3.1.4. PECVD Configurations

Generally, the PECVD configuration can be divided into Direct-PECVD and Remote-PECVD according to the position of the substrate relative to the plasma source.

1.1.1. Direct-PECVD



Figure 13. RF-PECVD is the typical direct-PECVD. SiH₄ and other gas reactants will be ionized and excited directly between the electrode plates.

In direct-PECVD (Figure.13), all the reacting gases are ionized and excited directly in the plasma region and the substrate is immersed in the plasma, so the ions and radicals reach the substrate by the means of the intrinsic DC bias in sheath. The PECVD using Capacitively Coupled Plasma (CCP) is the general type of direct-PECVD where the substrate is placed on one electrode plate to directly touch the plasma. In CCP reactors the RF-plasma power frequency at 13.56MHz is commonly used. The operating pressure is kept at 10-1000mTorr. The plasma density can reach from 1e⁺⁹ to 1e⁺¹¹ cm⁻³ with electron temperature ranging from 1-10eV. It has been found that in direct-PECVD the ion bombardment is inevitable because of the voltage bias between the plasma and the electrodes. Therefore, in direct-PECVD the ion bombardment is usually strong enough to induce damages to the film deposited.

The ion bombardment is inversely proportional to the frequency of the RF power supply. This is because the electrons driven by higher frequency RF power do not obtain enough kinetics before they collide with molecules in the plasma. Therefore the plasma density using higher RF frequencies is relatively low and the ion energy distribution is narrow. So this will cause less ion bombardment so the film density is lower. On the contrary, plasma excited by low RF frequency power will have higher plasma density for low power and

broader ion energy distribution. This will result in a stronger ion bombardment, which produces denser films and the films show compressive stress.

The equipment in direct-PECVD mode is easy for manufacture and the techniques used in RF-CCP are well developed in industry. Low frequency power supplies, down to kHz, can be easily implemented. Combining low and high frequency power sources one can easily adjust the stress in the films deposited.

3.1.4.1. Remote-PECVD

In remote-PECVD, the substrate is placed outside the plasma active region therefore only the secondary plasma can reach the substrate. The secondary plasma is the downstream plasma that diffuses from the primary plasma directly formed in the active region of the plasma, and the ion-excited molecules generated by downstream reactive ions on the substrate surface. SiH₄ will not be directly excited in primary plasma but be excited by the secondary plasma. The ions, radicals and electrons in the secondary plasma will have less kinetics than those from the primary plasma so there will be not many kinds of SiH_x^{*} ions species formed. So there will be fewer reaction paths to make it easier to control the film composition.

Due to the lower secondary plasma density, the effect of bias voltage is very weak and the ion bombardment can be reduced to nearly zero. Usually, a DC bias will be applied to extract ions to control the ion bombardment, deposition rate and film density. Therefore it is possible to independently control the plasma precursor excitation and the deposition rate.

In remote PECVD, the high-density primary plasma is necessary to generate precursors near the substrate surface. In Figure 14, a microwave source with frequencies over 1 GHz (usually 2.45 GHz at electron resonance) or an Inductively Coupled Plasma (ICP) source is usually applied to generate high plasma density. Electron Cyclotron Resonance (ECR) using a static magnetic field (Figure.15) is also widely applied for high-density plasma in high frequency.




Figure 15. Inductively coupled PECVD[32]

Generally, He or Ar will be directly excited in the plasma reaction region by a high-density plasma generator. The He and Ar ions with higher energy can then ionize and excite reactant molecules near the substrate surface. Ar is the most widely used inert filling gas because it helps to generate and sustain the plasma. It has been found that Ar would induce gas-phase reactions, which will generate more particles impurities during deposition. On the contrary, He with its lower atomic mass has less gas-phase reaction so fewer particles are generated. However, the plasma generated in He at low pressure becomes more difficult to sustain than using Ar.

G. Lucvosky and his research group developed the remote-PECVD configuration for improving a-Si (Ge) and dielectric gates deposition for the semiconductor VLSI industry. They found out that the most significant advantage of Remote-PECVD [34] is that the SiH₄ is not directly excited in the primary plasma region by electrons, but by metastable gas species (secondary plasma). So the SiH₄ is likely to be selectively excited or consumed. Therefore, using this deposition technique, it is possible to reduce the number of different ion/excited Si precursors, which leads to complicated reaction paths. People usually use N₂O, O₂, H₂ and NH₄ mixed with Ar or He to be directly excited in the primary plasma. Then a showerhead is used for

33

the SiH₄ inlet, which is excited by the primary plasma ions. The SiH₄ precursors formed by primary plasma contain specific ion/excited molecules making it easier to control the film quality by adjusting parameters such as substrate temperature, plasma frequency and power, flow rate and ratio.

Comparing films between Direct-PECVD and Remote-PECVD, it was found that the dielectric films (SiO₂ and Si₃N₄) are stoichiometric when produced by remote-PECVD and that films deposited by Direct-PECVD contains a large amount of Hydrogen atoms and no stoichiometry bonds (Si-Si) [34]. This is attributed to the differences of plasma excitation and inert gas (He, Ar) applied.

3.1.4.2. Microwave-PECVD

The Silicon rich oxide layers in this thesis were deposited by a Microwave-PECVD (AK400) from Roth & Rau manufacture, Germany (Figure 16). This MW-PECVD is regarded as a semi-remote PECVD because it consists of two plasma sources and one radio-frequency (RF) plasma source. Two quartz tubes with antenna inside can generate high-density plasma with 2.45GHz microwave. The two quartz tubes are placed 10cm over the substrate holder with RF plasma source connected. The 13.65MHz RF plasma source is generally used to generate bias voltage to control the deposition rate and ion bombardment. The two plasma quartz tubes are specially designed with the RF bias to produce a linearly extended plasma region. The reason why it is a semi-remote PECVD is that the plasma generation region and the reaction region are close to each other in the same chamber. So the SiH₄ is not totally separated from primary plasma region. But it utilizes the remote excitation of SiH₄ by using showerhead and top excitation gas feed-in structure. It is able to reduce the direct excitation of SiH₄ so it is possible to separately control the plasma density and deposition rate by bias voltage as Remote-PECVD does. Meanwhile, it is able to maintain a high deposition rate with higher excitation power.



Figure 16. Schematic MW-PECVD layout.

The microwave MW plasma power is able to reach 2000W at maximum. But 2000W is too high for the coupling circuit to maintain a reasonable reflected power and make the two plasma tubes work at the same power level. So only up to 1000W will be used for high-density plasma. Low plasma density can reach as low as 300W but it was found not enough to produce stable plasma, especially for low reaction pressure at 0.05 mBar. More general parameter values can be found in Table.1.

Parameters	Values
Temperature	200-400C
Base pressure	2e-4 mBar 0.15 mTorr
Process pressure	0.1 or 0.05 mBar 75 or 38 mTorr
MW Power	300-1000W
RF Bias	20-30V (30-50W)
Argon flow	50-100 SCCM
SiH4 flow	5-35 SCCM
N2O flow	5-60 SCCM

Table 1. General values for the parameters of the MW-PECVD

The RF power coupled with a RF matching network can generate up to 150V bias voltage by maximum power of 300W. In order to reduce the ion bombardment degradation and achieve a low deposition rate, turning off RF generator is helpful. However, it suffers from the severe non-uniformity due to the unstable plasma without an external electrical field. So low RF power at 30W-50W for 70V bias is necessary to balance the deposition rate and uniformity.

The substrate temperature can be varied from 200° C to 400° C. The chamber base pressure can reach $2x10^{-4}$ mBar. But it takes about 2 hours to reach the $5x10^{-5}$ mBar due to that the system has no load lock chamber. The reaction pressure can be controlled from 0.2 mBar to 0.05 mBar for general use.

The available reaction gases include SiH₄, N₂O, NH₃, Ar and H₂. The SiH₄ can only be filled in through the showerhead around the substrate. The user can choose to feed-in Argon, N₂O, NH₃ or H₂ from the top gas inlet or from the

showerhead. Therefore it is possible to get low ionization degree of gas oxidants if use showerhead as oxidant inlet.

For depositing Silicon rich oxide, SiH₄, N₂O and Argon were used. Normally, Argon and N₂O were fed in through top gas inlet. Then the high density of plasma ion mix reaches SiH4 near the substrate. The basic parameters of the MW-PECVD are summarized below.

3.2. Characterization techniques for SRO

In the previous section, the literature review on PECVD deposition including plasma basics, PECVD configurations, parameters and gas precursors for SRO deposition was presented. This section will review the optical and structural characterization techniques, including FT-IR, Raman, XRD, XRR, PL, for the understanding the SRO films.

3.2.1. Fourier Transfer Infrared Spectroscopy (FTIR)

3.2.1.1. FT-IR Introduction

Fourier Transfer Infrared Spectroscopy (FT-IR) is a fast and versatile technique widely applied for solid, liquid or gas materials for chemical structure detection. By identifying the specific Infrared light Absorbance/Transmission peaks, the information of specific chemical bonds or molecular groups can be revealed. The accurate measurement on IR Absorbance/Transmission intensity also makes it possible to calculate the specific chemical bond concentration [35].

Unlike the common optical spectroscopy that uses monochromatic light to measure the absorption for each wavelength by means of a monochormator, FT-IR applies a Michelson Interferometer combined with Fourier Transform calculated by a computer to quickly convert interferograms to the absorbance results (Figure.17). Therefore, white IR light can be used rather than laser or monochormator. One measurement over the full spectrum is done in a matter of seconds. The measurement can be performed multiple times to increase the signal to noise ratio.



Figure 17. It is the schematic structure of Michelson Interferometer. The sample is placed before the beam splitter. The light with Transmission information will be split to one fixed mirror and on translating mirroe. The translating mirror periodically oscillates to produce the interference at the beam splitter. The interferogram detected will be converted to Transmission spectrum by Fourier Transform.

Generally, FTIR is performed in transmission mode such that the transmitted infrared light through the sample in the normal direction will be detected. The absorbance is converted.

$$A = ln\left(\frac{1}{T}\right)$$

However, in some cases the absorption is too weak to be easily detected, as in the case in thin film materials of if surface scattering is strong, in such cases the Attenuated Total Reflection (ATR) or integrated sphere will be used to increase the signal.

3.2.1.2. Absorption Spectroscopy of SRO

FT-IR uses infrared light with wavelength ranging from 2.5um -25um or 400 – 4000 cm⁻¹ in wavenumber (cm⁻¹), which means the light frequency is from 10^{12} – 10^{14} Hz. The chemical bonds or molecular groups in the material characterized can be modeled as oscillators consisting of atoms connected by springs. These oscillators can vibrate in a specific frequencies f_k ranging from 10^{12} to 10^{14} Hz [8], which is in the same range of the infrared light frequency. In the simple diatomic spring model equation, m_r is the effective mass and k is the effective vibration strength.

$$f_k = \frac{1}{2\pi} \sqrt{\frac{k(m_1 + m_2)}{m_r}}$$

As the light is electromagnetic wave, the infrared light can interact with the chemical bonds or molecules with specific vibrating frequency in resonance. As a result, the infrared light is selectively absorbed by the specific dipole chemical bonds.

Chemical bonds can vibrate in different modes. For example, O=Si=O bond can vibrate in stretching, rocking or bending mode symmetrically or asymmetrically. The molecular vibration modes in specific frequencies interact with the infrared light with similar frequencies. Therefore by checking the absorbance peaks pattern it is easy to diagnose the existence of specific chemical bonds or molecular groups. Additionally, for organic materials, comparing the C=C and C=H intensity also helps to determine the Carbon chain structure.



Figure 18. Three Si-O vibration modes are illustrated as Stretching, Rocking and Bending [15].

FTIR has been generally applied to characterize SiO_x thin film materials. Three main vibration peaks are shown in Figure.18, representing Si=O stretching, bending and rocking modes, can be found in the regions of 1050-1080cm-1, 800-815cm-1 and 460-465cm-1 respectively. Besides, the impurities like H and N can also form Si-N or Si-H bonds, which can show obvious peaks in the measured FTIR absorbance. These impurity bonds are inevitably formed in PECVD due to the use of SiH₄, N₂O and NH₃ for SiO₂ and SiN_x layers. The absorption peak positions are summarized in the Table.2 [16].

Vibration modes	Wavenumber cm ⁻¹
Si-O stretching (TO)	1045-1090
Si-O stretching (LO)	1150-1200
Si-O bending	800-805
Si-O rocking	460-465
Si-N stretching	830-890
Si-H stretching	2000-2300
Si-H wag-rocking	630-650
N-H stretching	3340

Table 2. General IR vibrations in SRO materials produeced by PECVD.

Due to the complex bonding network in sub-stoichiometric films, the frequency for the specific bonding mode will show a shift in the absorption peaks. Locvsky et al. has reported the linear relationship (Figure.19) between the silicon richness and the Si=O stretching mode peak shift [43]. The linear relation between Si=O stretching peak and stoichiometry x in SiOx can be described as y=70x+930 (cm-1). Different researchers also verified this relationship indicating that more Si atoms involved in the Si=O network will change the Si=O vibration frequency [15].



Figure 19. The linear relationship between the stoichiometry and Si-O stretching mode peak shift from Locovsky [43].

However, when N is involved in large amounts, it is difficult to independently identify the Si=O peak and Si-N peak. Therefore, it is not reliable to use the linear equation to just discussed to evaluate the SRO stoichiometry. In this

case, a more involved interpretation of the films' absorbance is necessary to extract useful information on the chemical structure.

3.2.1.3. Data Processing and Sample Requirements

Baseline correction is necessary for data processing because there is always an offset in the FTIR absorbance spectrum. There are several factors determines the baseline shift, such as scattering, reflection and apparatus configuration. Scattering usually happens when the wavelength of the light used is comparable to the dimensions of particles or surface roughness on the sample that produce a stronger scattering for IR light with higher wavenumbers. This effect therefore shows a linear or curved baseline descending from high wavenumber to low wavenumber in the absorbance spectrum. On the contrary, the reflectivity becomes stronger for IR light with lower wavenumbers, which will show a rising baseline from high to low wavenumbers.

Besides being able to use the absorbance peak position can be used to indicate the chemical bonds, it is common practice to integrate the area under the peak to empirically evaluate the bond concentration [43]. However, this method is very dependent on experience and requires a calibration by highly accurate mass spectroscopy like SIMS, RBS or XPS.

For FTIR in transmission mode, it is important to use non-absorbing and nonscattering substrates where the thin film is deposited. Considering a material with low reflectivity and low absorption in IR region, KBr is the ideal substrate. But KBr is not usually available in laboratory. Additionally, the KBr substrate cannot withstand high temperature annealing over 750°C. Therefore, Si wafers become a good alternative substrate for its low absorption in the finger print region (400-2000cm⁻¹).

There are several requirements for the Si substrate:

- Double-sided polished Si wafer is preferred to avoid surface scattering causing signal loss.
- Low doping Si wafer (>10 ohmic.cm) is necessary to prevent free carrier absorption.

• Si has a high refractive index so the reflectivity is higher. Therefore, baseline correction for reflectivity is usually necessary.

Another issue is the CO₂ and H₂O absorbance in the range between 1400 cm⁻¹ – 1800 cm⁻¹. Usually, N₂ purging is applied to eliminate the CO₂ and H₂O vapor in the chamber. N₂ has non-polarized bonds so it is an inert gas transparent in IR making it ideal for purging. So N₂ purging in the sample chamber for 5-10 minutes before measurement will give clear measurement.

3.2.2. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is able to measure the atomic composition relying on the photoelectric effect. The incident X-Ray photon with a high energy can kick out the bound electrons in the atom. The electrons have specific binding energy in the specific atom. The kinetic energy of the electrons kicked out is able to indicate the atoms contained in the material.

Binding Energy (eV) =Photon Energy (hv) –Kinetic energy (eV)

XPS is a surface characterization technique and the sampling depth is only 2-5nm. Therefore, it is possible to do depth profile detection by using Ar sputtering. XPS is able to detect all elements except hydrogen atom and the detection limit can reach 0.1 at% at best. XPS not only can directly give the evidence of the existence of specific atoms, but it is also capable of identifying the atomic ratio.

When XPS peaks (Table.3) are carefully analyzed, narrower peaks can be observed, which unveil the molecular complexity and bonding information. In silicon rich oxide materials, the Si 2p core level with 99-103 eV binding energy is significant and can be used to determine the Si chemical composition. The Si atom in different bonding environments will have specific binding energy:

Table 3. XPS Si2p level charateristic binding energy		
Si covalent ion	Binding energy	
	(eV)	
Si ⁰	99	
Si ⁺¹	100	
Si ⁺²	101	
Si ⁺³	102	
Si ⁺⁴	103	



Figure 20. Deconvolution of Si-2p level to indicate the chemical structure in the material [23].

Generally, the Si⁺⁴ peak dominates the Si 2p level XPS peak in Silicon Dioxide. As demonstrated in Figure.20, the increasing Si content in Silicon rich oxide makes the Si 2p level peak down shift towards 101 eV, due to increasing amounts of Si³⁺, Si²⁺ and Si¹⁺ atoms. By careful deconvoluting of the main peak, it is possible to evaluate the composition of various Si bonding environment. Meanwhile, another XPS peak usually shows up at the binding energy of 99 eV meaning the formation of Si-Si bonding [23]. This is a direct evidence of excess Si, but it is not able to identify whether it is in crystal or amorphous form.

3.2.3. Raman Spectroscopy

Raman Spectroscopy is another vibrational spectroscopic technique for chemical and structural characterization. Rather than using high energy X-ray in XPS or IR in FTIR, Raman measurements use a laser with a specific wavelength (IR, visible or UV range) shone on the sample. The emitted (inelastically scattered) photon energy is then measured. The energy shift provides the information of vibrational and rotational transition in the material, which can indicate the chemical composition.

The laser photon is able to excite the molecule/atom to high energy states, then the molecule will go through a Rayleigh, anti-stroke or stroke energy

43

release process, which will emit another photon with no energy shift, or up or down energy shift by a specific value. The energy shift is caused by the inelastical interaction between the photon and a phonon. The interaction involving optical phonons is called raman scattering, and the involvement of acoustic phonon is called brillouin scattering.

Raman is usually used to detect crystalline Si formation in silicon rich oxide after high temperature annealing. A green laser with 514nm wavelength is usually used as the excitation light source. A sharp peak at 520cm-1 Raman shift will appear if there is c-Si. There is usually a broad shoulder besides the c-Si sharp peak from 500cm-1 to 230cm-1. It is assumed to be from the Si in amorphous state. Although there is still no one convincing result about the detailed analysis on this region by peak deconvolution, it is very certain that the 520cm-1 Raman shift indicates the existence of crystalline Si. The c-Si Raman peak shift is reported to be proportional to the compressive stress occurring in nano-crystalline Si (nc-Si), therefore the size of the nc-Si, to some degree, can be estimated by the peak shift [45]. In Figure.21, it summarized the size of dot by evaluation of Raman shift by different researchers.



Figure 21. Park investigated the effect of Raman shift due to the Si quantum dot size. It chould be caused by grain size and stress [44].

3.2.4. X-ray Diffraction (XRD)

X-ray with wavelength ranging from 1nm down to 0.1nm makes it possible to probe the structures of a similar size. X-ray Diffraction (XRD) is the most significant nondestructive characteristic technique to investigate the micro- or nano-crystalline structure in material. The application of XRD has been widely developed in mineral, organic, semiconductor and pharmaceutical material science. Generally, the crystal material identification, crystal degree and orientation, nano-crystal size and distribution are the main purposes of XRD application. It is also possible to evaluate the micro-strain, texture, lateral or vertical inhomogeneities. Therefore, XRD is a very powerful characteristic technique to investigate the nanocrystals.

In XRD, the X-ray beam is collimated and incident on the specular sample surface. The diffracted X-ray might be detected at different angles only if Bragg's law is satisfied.

$$2dsin(\theta) = n\lambda$$

Where d is the atomic plane distance, θ is the angle between the X-ray and atomic plane, and λ is the X-ray wavelength.

In a typical XRD experiment, material powder is under test by Bragg-Brentano XRD method to unveil all the diffraction peaks from the materials contained. However, this method is not applicable for thin film materials, especially when there are few crystals in nanometer range. In this case, the Glancing (or Grazing) -Incident XRD (GIXRD) method is necessary to maximize the diffracted signals. Figure.22 shows the differences of Bragg-Brentano XRD method and Glancing-Incident XRD (GIXRD).

45



Figure 22. (a) Bragg-Brentano XRD and (b) Glancing-Incident XRD. For thin film characterization, GIXRD is more useful to generate more information from the thin film.

For SRO with nc-Si, when using GIXRD there are usually visible 3 peaks from the $20 - 70^{\circ}$ in GIXRD 2θ scan results, which represent the Si crystal phase (111), (220), (113) respectively. It has been found that high temperature annealing at 1100°C for 1 hour is necessary to make the Si precipitate to form nc-Si. The XRD signal becomes stronger with longer annealing time indicating an increasing number and size of nc-Si in the material.

The nc-Si size can be estimated by the Debye-Scherrer's equation. It has been found that the XRD diffraction peak becomes broader when the crystal size decreases to 100nm or lower.

$$L = \frac{K\lambda}{B\cos\theta_B}$$

Where, L is the crystal size, B is the integral breath or FWHM and λ is the X-ray wavelength. K is the Scherrer constant to be varied according to different shapes of crystals. The selection of K was amply discussed by Langford in 1978 [29]. Usually, K=0.89 is applied for spherical nc-Si size calculation.

- K=0.94 for FWHM of spherical crystals with cubic symmetry
- K=0.89 for integral breadth of spherical crystals w/ cubic symmetry
- K=1.03 for tetrahedral crystallites (100) peak
- K=0.81 for octrahedral crystallites (100) peak

In the case of Si QD with size lower than 5-6 nm, the XRD size calculated in Debye-Scherrer's formula is quite consistent with the size observed under

TEM. But the Debye-scherrer method will underestimate the size if the crystal size increases to 10nm or larger. This is because of the micro-strain, which represents the inhomogeneous lattice distortion.

Besides the crystal size, the micro-strain and instrument can also contribute to the peak broadening. Linear and least square relationships can be used to fit the broadening [49].

$$B(2\theta) = \frac{\kappa\lambda}{L\cos\theta} + 4\varepsilon_0 tan\theta + B_i \text{ (Linear)}$$
$$B^2(2\theta) = \left(\frac{\kappa\lambda}{L\cos\theta}\right)^2 + (4\varepsilon_0 tan\theta)^2 + (B_i)^2 \text{ (Least Square)}$$

Generally, the least square fitting is used due to the fact that the size and microstrain have different angular relationships. In the equations, the parameter ε represents the microstrain degree and B_i is the instrumental broadening. The instrumental broadening can be calibrated for each angle and be eliminated in calculation. However, for the very small crystal size experiment, the contribution from the instrument is generally ignored [15].

3.2.5. X-ray Reflectivity (XRR)

X-ray reflectivity is able to characterize the thin film surface layer properties, such as thickness, roughness and material density. Most materials have a refractive index slightly larger than 1 for X-ray so that the X-ray can be totally reflected at glancing incident angle (0.02°). When the incident angle is larger than the critical angle, specular reflection shows up, which is dependent on the electron density change but not on the periodic electron density in the lattice. Hence, it is possible to measure both amorphous and the crystalline materials.

XRR uses the same equipment as XRD and there is no additional requirement for changing the configuration. Experimentally, glancing incident angle from 0.02-4 degree are typically used for 2Theta-Omega scan. Due to the high absorption of X-ray, longer integration time and smaller step size are necessary to achieve higher signal counts. A collimator will not be used and 1/16° divergence slit is commonly used to improve the resolution.



Figure 23. XRR finges can reveal informations about material density, thin film thickness, surface roughness and multilayer structure.

In Figure 23, many properties can be identified. The thickness measurement is the general purpose for using XRR. It is easy to evaluate the thickness by measuring the angular dependence of the oscillations. Typically, XRR is able to measure thin film thickness from 0.1nm to 1000nm. But due to the instrumental accuracy, 200nm is usually the limit for SRO thin film on Si or Quartz substrates. With this technique it is possible to measure monolayers as well as multilayer structures. XRR is sensitive to the thin layer thickness variation.

Besides the thickness measurement, another useful application of XRR is to evaluate the material density and interface roughness. Qualitatively, a sharp curve slope and a low oscillation amplitude indicate a high roughness and high material density because higher roughness increase the scattering and higher density increase the absorption so that the reflection intensity drops faster. Generally, software fitting is necessary to assist for the quantitative analysis. Good understanding, proper instrument configuration and knowledge of the sample structure are necessary to produce reasonable fitting result.

The use of XRR overcomes the difficulties in thickness measurement by encountered when using Spectroscopic Ellipsometry (SE) for SRO materials,

48

especially for the SRO after annealing. For thin film with a thickness less than 200nm, XRR give a reliable and direct result.

3.2.6. Photoluminescence

Photoluminescence (PL) effect originates from the radiative recombination in semiconductor materials, by which it is possible to probe the electrical and optoelectronic properties. For quantum dot materials, PL emission is the most immediate evidence of quantum confinement effect by PL. Many researchers worldwide generally reported a blue shift of the PL peak when reducing the quantum dot size. Different quantum dot materials were investigated and all show a similar PL effect, such as GaAs, InS and Si quantum dots.

As shown in the quantum confinement model, smaller QD size enhances the discrete electron energy levels therefore the effective bandgap should be larger and an emission of photons with higher energy (blue) is expected. By controlling the Si quantum dot size to 5nm, 4nm and 3nm (Figure.24), it was found that the PL emission peak shifts from 1.3eV, 1.37eV to 1.46eV [44].



Figure 24. Normallized PL peak blue shift when the Si QD size decreases from 5nm to 3nm [44].

The Photoluminescence equipment is relatively simpler compared to those needed for other characterization techniques. The basic PL equipment consists of one laser for excitation, sample holder, optical lens, filters to isolate the laser from the PL emission and a CCD detector. Usually, green and blue lasers will be applied to provide enough excitation energy. The

excitation modes can be steady state or transient, and they can be used to unveil the electronic structure in Si quantum dot in SiO₂ matrix.



Figure 25. Two PL peaks in transient PL measurement. The PL peak over 600nm is from the Si quantum dot. PL blue shift is shown for smaller Si QD size. The PL peak below 600nm is proposed from the direct recombination at Si Γ point enhance by auger recombination [12].

In practice, PL results usually do not obey the quantum confinement model, which indicates the complexity of energy band structure in Si QD. Boer and et al. intensively investigated the transient PL effect in the picosecond time range on crystalline Si quantum dots in SiO₂. The samples were fabricated by co-sputtering and subsequent 1100 °C annealing. They reported two kinds of PL peak in Figure.25. The peaks over 600nm, as normally believed as phonon-assisted recombination in Si, will undergo blue shift due to Si quantum confinement. The other peaks below 600nm which undergoes a red shift is attributed to the hot carrier radiative recombination with no phonon involved at the Γ point where the band gap is larger. Auger effect to enhance the electron injected into the effective conduction level (Figure.26) is essential for the direct recombination process [12].



Figure 26. Auger recombination enhance the PL intensity by a high photon flux [12]. Although PL is a very useful tool that indicates the optoelectronic structure of quantum dots, it requires very sophisticated understanding and careful explanations to interpret the results. There is still debate on the origins of the PL as some propose the emission is from the recombination at interface. Therefore, one should be careful when comparing PL results with other characterization methods.

Chapter 4. Experiment & Discussion

4.1. Monolayer SRO Deposition

In order to calibrate the deposition parameters for the MW-PECVD, monolayer SiO_2 and SRO thin films were deposited and characterized. The Si wafer or quartz substrates were used at the same time for different characterization techniques, such as Raman spectroscopy requires quartz substrate and FTIR requires the use of Si wafer. Generally, XRR was used to measure the thin film thickness and FTIR was applied to probe the chemical composition.

For the fabrication of superlattice, very low deposition rate is necessary to control the film thickness in a few nanometers. Meanwhile, it has to be able to adjust the silicon richness. Therefore, parameters including substrate temperature, MW plasma power, SiH₄ flow rate, SiH₄/N₂O ratio and Argon flow rate were investigated in detail to find the optimal values.

The deposition rate and the chemical composition were two main results used to evaluate the PECVD parameters. In this section, several groups of samples with obvious features will be presented to illustrate these parameters.

4.1.1. Substrate Temperature

Different substrate temperatures from 200 to 300C were applied to evaluate the substrate temperature effects on the SRO films. For higher silicon richness, SiH4: $N_2O=5:5$ (SCCM:SCCM) was used. The MW plasma power was 500W at the reaction pressure of 0.05 mBar. Low RF bias at 70V was applied to maintain the uniform electric field on substrate to keep high film uniformity.

Temp. (C)	RATE (nm/min)	Si-O stretching	Stoichiometry
,	. ,	mode cm-1	of SiOx
200	18.36	1040	1.6
250	15.51	1020	1.4
300	15.25	1000	1.0
NA	NA	1066 (SiO ₂)	2

Table 4. Substrate temperatures and its effects on Si-O stretching mode shift and stoichiometry of SiOx. $(SiH_4/N_2O=5/5)$

The deposition rate will decrease when the substrate temperature increase (Table 4). This is controversial to the general experience that higher substrate temperate should increase the deposition. However, the substrate temperature has minor effect on the deposition rate when the temperature is higher than 250 °C.



Figure 27. FTIR result for different substrate temperatures. Three Si-O characteristic peaks can be identified shifted from 1060cm⁻¹. The dashed curve is the SiO₂ result as reference. The 1107cm⁻¹ is due to the oxidation in the air.

In terms of composition, it can be seen that three characteristic peaks representing the rocking, bending and stretching Si-O vibration modes are clearly shown in Figure.27. More importantly, it shows that the Si-O stretching TO mode around 1060cm-1 shifts to lower wavenumber values with increasing substrate temperature. According to Locvosky and his research fellows [35], the shift is proportional to the silicon richness so it is possible here to evaluate the silicon richness by the empirical equation described in Chapter 3.1.3.



Figure 28. The left graph shows the linear relationship between the Si-O stretching mode peak and stoichiometry. The substrate temperature influences the film composition remarkably. There is a linear relationship between the temperature and the stoichiometry.

In quick summary, higher temperature reduces deposition rate but increases the silicon richness simultaneously (Figure.28). Comparing to the deposition rate, the stoichiometry changes remarkably with different substrate temperatures. The substrate temperature is not the preferable parameter to use to adjust the stoichiometry or the deposition rate.

Generally speaking, the high quality SiO_2 with higher density and low defects as barrier layer is usually achieved at 400 °C. Therefore the use of higher temperature (400 °C) is preferred for superlattice structure fabrication as the confinement to form Si QD during 1100°C annealing is important.

4.1.2. MW Plasma Power

The effect of MW plasma power to the deposition rate and chemical content was briefly investigated by a group of samples fabricated under different MW plasma power conditions. The conditions are summarized as below.

MW plasma power.		
Parameters	Values	
Temperature	400	
MW Plasma power	300W 700W 900W	
Reaction pressure	0.1 mBar	
SiH ₄ : N ₂ O: Argon	10:5:50 (SCCM)	
RF bias	70V	

Table 2. Parameters for samples fabricated using low to high MW plasma power.

Higher SiH₄ and higher reaction pressure were used for higher Si richness. 400°C substrate temperature was used and 70V bias was still applied for better uniform film.

Power	Rate (nm/min)	Main Peak (cm ⁻¹)
300W	27.3	852
700W	25.0	928
900W	24.8	947
SiO ₂	N/A	1066

Table 3. Deposition rate and FTIR Si-O stretching mode peak position. (SiH (N) O = 10(10))

The deposition rate was found to be around 25nm/min, which is almost doubled comparing to the samples for substrate temperature (average 16 nm/min). It is mainly due to higher SiH₄ flow rate (Chapter 4.1.4). Higher MW plasma power will induce slightly lower deposition rate that the increase of power from 300W to 900W only reduce the deposition rate from 27.2nm/min to 24.8nm/min. So power is not the significant factor for deposition rate.



Figure 29. FTIR results show that SiH4: N2O=10:5 introduces too much N in the film. The higher power tends to make the film contain more Si-O bonds.

However, the FTIR result in Figure.29 shows that there is a dramatic peak shift for the Si-O stretching mode. This shift is not because of excess silicon in the film, but it is mainly due to the Si-N asymmetric stretching mode between 830 - 890 cm⁻¹.

For higher power of 900W, the film contains more Si-O bonds since there are still three peaks visible at 450cm-1, 800cm-1 and 980cm-1. But when the power drops, the main peak shift indicates that more Si-N dominates the IR

absorption. For 300W and 700W samples, the asymmetric main peak is attributed to the combination of Si-O stretching mode and Si-N stretching mode.

This Si-N IR absorption dominating effect can only be observed when the SiH₄ $/N_2O$ flow ratio is high. In this case, the empirical linear relationship between FTIR peak shift and silicon richness from Lucovsky and et al. (Figure.17) is not valid anymore. Therefore XPS will be a useful tool to accurately indicate the silicon richness.

Too low power, as 300W, will involve too much Nitrogen in the film so it is not preferable for SRO deposition. It is conceivable that higher power can maintain to generate more O* ions to form Si-O bonding so more Si-O bonds can be observed. The large N involvement might be due to the incomplete N_2O dissociation to form NO.

As a result, 900W becomes good value for lower deposition rate and lower Nitrogen involvement. Making MW plasma power constant will make it easier to adjust other parameters for relatively lower deposition rate and more importantly desired lower N concentration.

4.1.3. Argon Flow Rate Influence

Argon, working as inert gas to enhance the plasma ionization, was used in the experiment. Higher Argon flow rates over 50 were used and the SiH4: N2O flow rates ratio was kept as 5:5 SCCM (Table 7).

Parameters	Values
Temperature	400C
Plasma power	900W
Reaction pressure	0.1 mBar
SiH ₄ : N ₂ O: Argon	5:5:80/110/140 (SCCM)
RF bias	70V

Table 4. Sample fabrication parameters for Argon flow test.

The deposition rate will increase slightly with increasing Argon flow rate and fraction. So Argon should be the minor factor to the deposition rate (Table 8).

Argon flow rate	Rate	Si-O stretching
(SCCM)	(nm/min)	peak (cm⁻¹)
80	13.9	1066
110	14.1	1062
140	14.5	1062

Table 5. Deposition rate and Si-O stretching peaks for Argon flow test. (SiH₄/N₂O=5/5)



Figure 30. SiH₄:N₂O=5:5 SCCM with higher Argon has higher Si-O content and lower Si richness. Argon enhances N₂O dissociation. But higher Argon flow also induces surface roughness from the baseline showing stronger scattering.

The three peaks shown in FTIR result (Figure. 29) indicate SiO_2 films were obtained. The Si-O peak positions for various Ar flow rates are identical, which means the samples have the identical chemical composition. The Si-O stretching mode does not shift to lower wavenumber greatly. So there should be less Nitrogen involved (4.1.2).

Another piece of important information from the baseline in Figure.29 is that the sample fabricated by higher Argon shows stronger scattering effect because the baseline slope rises up to higher wavenumber. The stronger signal loss for short wavelength light scattered is due to surface roughness.

Generally, the reflectance effect will make the FTIR result of SiO_2 or SRO with less surface roughness have a descending baseline. So in our case, it

indicates that the films suffered high bombardment by higher Argon flow and the surface roughness should be high. AFM will be useful to identify the prediction.

Therefore, increasing Ar flow rate is able to increase the deposition rate but not to change the composition significantly. This indicates Ar is the parameter to slightly adjust the deposition rate. Although the surface roughness could be a issue, in terms of Si QD formation, high temperature at 1100C makes the roughness or thin each layer inferior factor to consider.

4.1.4. SiH₄ Flow Rate to Deposition Rate

By summarizing the deposition rate in terms of substrate temperature, Argon flow and MW plasma power in table 9&10, it was found that the SiH4 flow rate was the direct and most significant factor determining the SRO deposition rate in AK400 remote plasma PECVD system.

By revising the Table 4&6&8, the deposition rate variation was not significant with various temperature, Argon and MW plasma power parameters respectively. But in these experiments, SiH4/N2O ratio was controlled as 1 (Table 9). The deposition rate increased dramatically with higher SiH₄ and N_2O flow rates.

Parameters	Average Deposition Rate (nm/min)	
Temperature: 200/250/300 °C SiH ₄ /N ₂ O=5/5	16.4	
MW Power: 300/700/900 W SiH ₄ /N ₂ O=10/10	25.7	
Argon flow: 80/110/140 SCCM SiH ₄ /N ₂ O=5/5	14.2	

Table 6. PECVD deposition rate SiH_4/N_2O ratio test.

Another example is the comparison between the SiO_2 and SRO on deposition rates. The rates are almost the same for using constant 10 SCCM SiH_4 (Figure.10). The different N₂O flow rates made different total flow rates but there was slight rate variation. This suggested that the total flow rate is not the critical factor determining deposition rate. But only the SiH4 flow rate is.

Therefore, to control the deposition rate, SiH4 is the prior parameter to adjust for determining deposition rate. Other parameters, such as Temperature, MW power, Argon flow and total flow rate, are minor factors to modify rates.

Deposition parameters	Deposition rate (nm/min)	
SiH ₄ : N ₂ O:Ar =10:50 :50 – SiO2	25.32	
SiH ₄ : N ₂ O:Ar =10:5 :50 - SRO	24.52	
400C substrate temperature		
0.05 mBar pressure		
65V bias voltage		
500W plasma power		

Table 7. SiH₄ flow rate dominates the deposition rate.

The reasons that the deposition rate was proportional to the SiH₄ flow rate might be the high-density MW plasma and gas feed-in mode.

In the MW-PECVD, the SiH₄ was fed in through the showerhead around the substrate but not fed in with the Ar and N₂O from top passing through the plasma activation region (Figure 25). High-density plasma (containing Ar* and O* ions/excited species) by high power microwave excitation can fully excite the available SiH₄ to start reaction. Therefore, the higher SiH4 availability comes with higher deposition rate.

4.1.5. SiH₄/N₂O Ratio to Composition

The SiH₄: N₂O ratio mainly changes the composition in the film. By fixing the SiH₄ flow rate to 10 SCCM, N₂O was varied from 2 SCCM to 50 SCCM to obtain different SiH4: N2O ratio.

In Figure.31, for the samples having 1:1 or lower ratio, there are Si-O bonds in the film as indicated by the three Si-O mode peaks. The Si-O stretching mode peak shift indicates a higher Si richness. The Si-N mode becomes dominating when SiH₄:N₂O>1, for instance as seen on the sample with SiH₄:N₂O=2 and 5. The asymmetric main peak is believed to be due to the combination of Si-N asymmetric stretching mode peak and shifted Si-O stretching mode peak.



Figure 31. FT-IR result of SiO_x sample fabricated by different $SiH_4:N_2O$ ratio.



Figure 32. Higher SiH₄:N₂O ratio increase Si-H bonds and N-H bonds. But further increase in SiH₄ makes the Si-H decrease.

It is also possible to use other FTIR IR peaks to identify the H and N involvement. The peak at 2200cm⁻¹ indicates Si-H bonds and the peak at 3300-3400 cm⁻¹ indicates N-H bonds in Figure.32.

For over flowing N_2O , SiO₂ film can be achieved with no detectable Si-H and N-H bonds. Increasing SiH₄ ratio brings more Si-H bonds and N-H bonds,

which means there is a higher Si and N involvement. But further increasing the SiH₄ ratio will reduce the Si-H and only increase N-H bond.

Therefore, to have relatively higher Si richness, the ratio of 10:10 is optimal without adjusting MW plasma power or Ar flow rate. This ratio brings less N-H bonds and higher Si-H bonds.

4.1.6. Uniformity Improvement

Film uniformity is important and critical for the thin film superlattice deposition because the layer thickness determines the nc-Si size. Low deposition rate, uniform bias voltage and initial surface conditions will help to improve the film uniformity.

During the SiO₂ and SRO film deposition on Si wafer by MW-PECVD, it was found that SiO₂ is very sensitive to the initial surface condition. So surface processing before deposition can improve the uniformity. HF dip without rinsing can make the Si wafer substrate surface passivated with Hydrogen. So the uniform H-passivated surface can give very good film uniformity. Another method to improve uniformity is by using Argon plasma flush, which is usually used to remove contaminants on the substrate surface [9], especially effective for removing organic particles. Ar can also remove the residual gas from previous depositions.

Bias voltage is important for remote PECVD. A low bias voltage maintains an electric field to attract ions that arrive uniformly on the substrate. It was found that without the bias the film uniformity was significantly affected.

Basically, lower deposition rate at lower pressure can also improve the uniformity because there will be less SiH₄ concentration gradient along the surface.

4.2. Superlattice Deposition

4.2.1. Pulse Deposition Method for Thin Film Deposition

Unlike RF-Sputtering, PECVD is designed to have relatively higher deposition rates. So a very short time is needed to deposit an extremely thin layer. In practice, the thin film deposition conditions aiming to obtain 4-10nm thick films

61

are different from those to deposit thick monolayers. According to the deposition rate calibrated for the monolayer in previous sections, only 9-10 seconds are needed to deposit a 4nm thin film when using 10 SCCM SiH₄ as shown in the plasma power calibration. The actual deposition rate over a very short deposition time is much faster than the rate calibrated for the monolayer in steady state condition. As a result, much thicker layers than intended would be obtained with a 9-10 second deposition.

To understand this one needs to realize that the plasma requires a short time to reach a stable state. This stabilization process might take 10 to 20 seconds depending on the quality of the PECVD design. The deposition rate will then slowly decrease during the deposition. The result is that the rate calibrated is usually the average rate of the deposition under steady state conditions. To solve this problem, one can apply pulse deposition to control the thin film CVD deposition rate.

In this thesis, pulsed deposition means igniting the plasma for 3-5 seconds in order to achieve very thin layers. The basic PECVD parameters in pulse deposition have a similar influence on the deposition rate and composition as observed in the thick layer depositions. In order to investigate the pulse deposition, it is necessary to repeat the pulse deposition numerous times to accumulate thicker films for FTIR and XRR measurement.

The SiH₄ flow rate is still the main factor determining the deposition rate. A comparison between two samples using SiH₄: N₂O=5:5 and SiH4: N₂O=15:5 shows a higher deposition rate for the sample using SiH₄=15 SCCM. The duration of each pulse was 5 seconds. This pulse was repeated 20 and 30 times respectively. The other parameters were kept identical (400°C substrate temperature, 1000W power at 0.05mBar with 70V bias).

Table 8. The comparison between the pulse and the monolayer deposition rates	. SiH₄ is still
the main factor for deposition rate.	

Parameters	Deposition rate	Monolayer rate	
SiH ₄ : N ₂ O=5:5	3.5nm/5s	15-18 nm/min	
(5s for 20 times)	42nm/min		
SiH ₄ :N ₂ O=15:5	6nm/5s	25-29 nm/min	

(5s for 30 times)	72nm/min	

The very high deposition rate might be partly attributed to the high transient RF substrate power. The RF power was very high at the beginning to help ignite the plasma together with the microwave. Therefore, this is equivalent to a direct PECVD using Capacitively Coupled Plasma (CCP) source so the SiH4 will be directly excited. Without using the RF source, it was found that the initial deposition rate decreased to 42nm/min from 72 nm/min in Table.10 when using 15 SCCM SiH₄. The high deposition rate of 42 nm/min could be attributed to the initial high microwave plasma power.

SiH ₄ : N ₂ O (SCCM)	Plasma Power (Time for periods)	Deposition rate	Deposition rate
5 : 5	1000W (5s for 20 times)	3.5nm/5s	42nm/min
15 : 5	1000W (5s for 30 times)	6nm/5s	72nm/min
25 : 5	350W (4s for 10times)	6.7/4s	100nm/min
30 : 5	350W (4s for 10 times)	Data not available	Data not available
35 : 5	350W (4s for 10 times)	7nm/4s	105nm/min
35 : 5	1000W (10s for 10 times)	17.8nm/10s	107nm/min

Table 9. Summary of pulse deposition rate.

4.2.2. FTIR & XPS for Pulse Deposition

Using the same PECVD parameters except for the repeated pulse disposition or the steady state deposition, a comparison is presented in this section. In the FTIR result (Figure.33), the main peak positions are 940cm⁻¹ for the steady state plasma and 860cm⁻¹ for the pulse deposition. So there should be more N in the SRO films by pulse deposition. More details are listed in Talbe.13.

Table 10. PECVE	parameters for sample tested b	y XPS and FT-IR.
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Parameters	SRO (Monolayer)	SRO (pulse)
Substrate temperature	400	400
(C)		

Plasma power (W)	700	700
Pressure (mBar)	0.05	0.05
SiH ₄ :N ₂ O:Ar	10:5:50	10:5:50
RF bias (V)	70	70
Time	5 mins	5s x10
Average Rate (nm/min)	25	72
FTIR main peak (cm-1)	930	850



Figure 33. Comparison between the FTIR results of samlpes fabricated by the pulse and the thick monolayer deposition.

In order to evaluate the N content in the film, XPS result in Figure.34 was applied to the SRO sample fabricated by pulse deposition. It was found that the typical SRO pulse deposition induces large amounts of Nitrogen in the film, which is even higher than the Oxygen content. The Nitrogen can reach as high as 25 at% and whereas Oxygen reaches only 20 at%. However, there is a high Si content reaching 55 at%. The XPS result of stoichiometric SiO₂ shows that there is very low Nitrogen content (average of 4 at.%). This immediately explains the FTIR main peak shift to 830cm-1, which must be caused by Si-N bonds.

By checking the Si 2p level in Figure.35, the peak at binding energy of 99 eV is very obvious. It is generally identified as an Si-Si bonds. The Si-Si bond is preferred for nc-Si formation. However, the main peak for Si 2p level is

located at 103 eV indicating a large amount of Si³⁺ exists. The shift from Si⁴⁺ to Si³⁺ is widely accepted as evidence of excess Si, H and N involvement.



Figure 34. XPS results for SRO. Large amount of N was incorporated in the SRO sample. The unstable plasma causes the concentration fluctuation.



Figure 35. Si-2p level shows Si-Si bond at 99eV binding energy and large Si³⁺ peak, which means the large amount of impurity (Si, N, H) involved.

4.2.3. SiO2/SRO Superlattice by Pulse Deposition

By applying pulsed deposition, a 10-bilayer (SiO₂/SRO) superlattice structure has been fabricated and presented in this section. The thin films were

deposited layer by layer on polished Si substrate. The SiO₂ and SRO films were also deposited on another two polished Si wafers with high resistivity respectively for FTIR characterization. For each SiO₂, SRO and superlattice sample, the pulsed depositions were repeated 10 times. The details are listed in Table.14.

Parameters	SiO ₂	SRO
Substrate temperature (°C)	400	400
Plasma power (W)	700	700
Pressure (mBar)	0.05	0.05
SiH ₄ :N ₂ O:Ar	5:25:50	10:5:50
RF bias (V)	70	70
Time (s)	5x10	5x10

Table 11.PECVD parameters for the SiO₂/SRO superlattice deposition.

According to the Bragg peaks in the XRR spectra in Figure.36, there must be distinct SiO_2 and SRO interfaces. The larger Bragg peaks indicate the SiO2/SRO bilayer thickness is 12.4nm. Between the Bragg peaks, 9 small peaks indicate 10 bilayers structure. The small fringes can give us the total thickness of 130.2nm, which is consistent with the total bilayer thickness plus a 10nm capping layer. Due to the signal intensity limit of the detector, the signal vanish quickly after the incident angle is larger than 0.9.



Figure 36. XRR result of the superlattice structure showing 130nm total thickness. For each bilayer, it consists of $6nm SiO_2$ and 6nm SRO.

FTIR was applied to characterize the SiO₂, SRO and superlattice structure respectively to be able to identify IR absorption peaks from different layers (Figure.37). The red dashed line is calculated based on the spectra obtained for the pulsed SiO2 and pulsed SRO thick layers and represents the combination of SiO₂ and SRO IR absorption. The multilayer IR absorption is consistent with the combined IR absorption.



Figure 37. FTIR results for SiO₂, SRO and superlattice. Si-O peak is mainly from the SiO₂ and Si-N from SRO. The Silicon richness is not very high because no Si-H at 630cm⁻¹ is shown.

The main peak at 1030-1040 is from the SiO₂ film. The SiO₂ film should be silicon rich oxide as SiO_{1.4} from Lucovsky's equation. Another peak around 850cm⁻¹ is mainly from the SRO layer. And it indicates there must be very high Nitrogen content. The broad peak in SRO from 700 – 1200cm⁻¹ indicates the complex in the SRO film consisting of Si-N, Si-O and Si-H bonds.

4.3. Annealing of SRO thin film

4.3.1. SRO Compositional Change by Annealing

The SRO film deposited with high SiH₄ flow rate (35 SCCM) was annealed to investigate the chemical change in the film. High temperature annealing at 1100° C and low temperature annealing at 480° C were carried out in an N₂ purging atmosphere. The annealing duration was fixed to 1 hour.



Figure 38. Comparison of FTIR results for the as-depo, 1100°C and 480°C annealing.

From the FTIR result in Figure.38, the 1100°C annealing for 1 hour completely changed the chemical composition in the film. The most significant effect is the reduction of Si-N bonds and the increase of Si-O bonds. This is indicated from the main peak shift from 830cm⁻¹ to 1060cm⁻¹. The broad shoulder between 800cm⁻¹ – 1000cm⁻¹ in the sample annealed at 1100°C means there are still Si-N bonds exist. The high temperature definitely eliminates all H related bonds in the film as the Si-H bond peak at 630 cm⁻¹ disappears. Further XPS test will help to elucidate if the chemical bond change is due to bond transfer from Si-N to Si-O or the oxidation of excess Si.

For the 480°C annealed sample, Si-H bonds disappear and a slight increase of Si-O is observed. The Si-N bond did not reduce markedly compared to the sample annealed at 1100°C. There is no evidence to correlate the slight Si-O increase to the dehydrogenation but there is research showing that H in a-Si will help Si-Si bond formation [51], which might indicate here that the loss of H bonds form Si-O bonds.

GIXRD was carried out on the sample annealed at 1100°C, showing that there are Si crystals formed in these films.

4.3.2. XRD & Raman Analysis on Si Crystallization
High temperature annealing at 1100°C for one hour was applied for nc-Si precipitation. Theoretically, the excess Si content in the SRO film should precipitate at high temperature. However, the superlattice sample annealed at 1100°C shown in section 4.1 did not show such Si precipitates as no XRD Si peaks were observed in GIXRD. The SRO film in the superlattice used SiH₄: N_2O ratio of 10:5.

Raman spectroscopy was also applied to detect the low content of c-Si formation in the superlattice. In Figure.39, the peak at 521cm-1 Raman shift was found indicating the existence of Si crystal. But the content should be low according to the lower peak intensity.



Figure 39. Raman result of the annealed superlattice sample shows c-Si peak. The red line is the Raman result for c-Si.

There is however, debate on the use of Raman measurements to detect crystalline Si as the focused laser beam might have high enough energy to cause the Si to crystallize. As a result of this, the c-Si observed might be not from high temperature annealing. During the Raman spectroscopy measurement, the laser power was kept at 0.25mW and a 50x objective lens was used. However one cannot fully rule out the possibility of laser induced crystallization.

In order to investigate the relationship between the SiH₄: N₂O ratio and c-Si formation, annealing was carried out on a group of samples fabricated under

different SiH₄: N₂O ratio conditions. GIXRD was used to detect the diffraction peak at 2θ =28.45, which should be a direct result of the formations of silicon crystals.

SiH₄: N₂O: Ar (SCCM)	XRD peak at 2 0 =28.45	Temperature: 400C Power: 1000W
5:5:50	No	Pressure: 0.05 mBar
15:5:50	No	Bias: 30-50V
25:5:50	Low	Pules: 5s
35:5:50	Medium	Periods: 20

Table 12, XRD test for finding the proper SiH4:N2O ratio for Si crystallization in SRO.

According to the results shown in Table.15, for SiH₄: N₂O lower than 3, there were no detectable Si crystals in the SRO film. This result suggests the difficulty of balancing the deposition rate and silicon richness because higher SiH₄ flow rate for higher silicon richness can dramatically increase the deposition rate so even smaller pules time is needed. Additionally, there will be a small parameter space to further reduce the N₂O flow rate down to 5 SCCM.



Figure 40, GIXRD result of the samples with increasing SiH4:N2O ratio.

More experiments were done to investigate Si crystallization. The SRO samples were deposited by 4-second Pulse deposition for 10 times on Si and quartz substrates. The thickness values were from 67 to 70nm. The power was 350W in order to reduce deposition rate and N content. The GIXRD results are shown in Figure.40.

Table 13. The estimation of nc-Si size from GIXRD result.

SiH ₄ : N ₂ O: Ar	XRD breath at	Temperature: 400C	
(SCCM)	20=28.45	Power: 350W	
25:5:50	3	Pressure: 0.05 mBar	
30:5:50	2.8	Bias: 20-30V	
25.5.50	2	Pules: 4s	
35.5.50	3	Period: 10	

By using SiH₄: N₂O > 5, c-Si peaks are clearly shown in XRD. The GIXRD was carried out with relatively low resolution so the noise is high. The three samples have similar 20=28.45 peak breath. To evaluate the nc-Si size, an approximation of peak breath of 0.052 radians (3 degree) is used for Scherrer's equation (Table.16).

$$L = \frac{K\lambda}{B\cos\theta_B}$$

K=0.89 was used to assume the spherical nc-Si shape. Then the average nc-Si size would be 2.72nm. This small value might indicate the low Si richness or that the Si aggregation might be hindered.

Chapter 5. Conclusions & Future Work

5.1. MW-PECVD for Thin Film Deposition

5.1.1. Deposition Rate

Compared to RF-sputtering used before at UNSW [14], the MW-PECVD has much higher deposition rate. However, it is possible to use a pulsed deposition method to deposit 3-6nm thin SiO₂ and SRO layers. As a result, alternating SiO₂/SRO to create a superlattice with distinct interfaces can be achieved according to XRR result (Figure.36).

It should be noted that it is more difficult to control the deposition of thin SRO layers with a thickness lower than 3nm, when using the MW-PECVD setup employed in this thesis. Although the MW-PECVD is enough for deposition for initial research and demonstration purpose, specially designed PECVD system (Section 2.2 Figure.8) for ultra low deposition rate will be ideal for material and device fabrication.

In terms of MW-PECVD, the main factor determining the deposition rate was found to be the SiH₄ flow rate rather than the pressure as originally expected. This might be because of the remote PECVD setup, which uses a SiH₄ showerhead gas inlet. In this configuration, the SiH₄ will determine the SiH₄ concentration near the surface hence it will determine the deposition rate. The pressure in the MW-PECVD is adjustable from 0.05mBar to 0.1mBar. This pressure range might be not large enough to affect the deposition rate. Other parameters, such as pressure, substrate temperature, total flow rate and Argon flow rate, influence the deposition rate slightly, but dramatically influence the SRO film quality.

5.1.2. Chemical Properties of SRO

The silicon rich oxide (SRO) films deposited by high SiH₄: N₂O was found to contain a high Nitrogen content. While increasing the SiH₄: N₂O ratio to obtain higher excess Si, there will be more N involved. According to FTIR and XPS measurements, the film becomes Si_{1-x-y}O_xN_y rather than SiO_x. The N content can be equal to the O content as 20 at% in the film for SiH₄: N₂O=7. This effect is similar to that reported in the literature by other researchers who use

RF-PECVD for SRO film deposition. Meanwhile, large amounts of Hydrogen will also be incorporated due to the use of SiH₄. The H can be found in the form of Si-H and N-H bonds according to FTIR.

Besides the SiH₄: N₂O ratio, another significant factor that should be considered is the plasma power. Higher plasma power tends to reduce the N content in the film. This is because a higher O* ions concentration will be formed. During plasma ionization, N₂O will be initially dissociated into NO* ions and N₂. NO* then further dissociate to form O* ions. The O* tends to react with SiH₃* or other Si precursors to generate SiO₂. If the N₂O cannot be fully dissociated, it is conceivable the films will have more N.

In order to reduce the N content, it might be helpful to use O_2 mixed with N_2O as the oxidant gas in MW-PECVD. Because more O* ions will be generated to increase Si-O bonds and N_2O will reduce the intense reaction from O_2 . However, using O_2 might increase the safety hazard in the laboratory.

Argon helps to ignite plasma and also reduces the power delivered to the dissociation of N_2O . Another drawback for using a high Argon flow ratio is the strong ion bombardment to the film. This is believed to increase the surface roughness (Figure. 29).

5.1.3. Fabrication Improvement

As the XRD results show (4.3.2, Figure. 40), nc-Si forms when using a higher SiH₄: N_2O ratio and makes it possible to fabricate superlattice structures to confine the nc-Si size. A higher Si richness is necessary as only 3nm nc-Si was achieved in the SRO films despite these films being 4nm thick.

In order to further increase the Si richness, higher SiH₄: N_2O ratio should be used. To compensate the higher deposition rate when increasing the SiH₄ flow rate, shorter pulse time should be used.

The SiH₄: N_2O is the main factor determining the deposition rate but, in order to have flexibility in the deposition rate without compromising composition, it is necessary to find another parameter that may help to control the deposition rate. Argon flow rate and ratio might be a good candidate for this aim because it has only a slight effect on the film composition. It should be noted that increasing Ar flow enhances ion bombardment, which could be an issue that needs to be investigated.

Besides using MW-PECVD, some more advanced deposition techniques should give better control and good film quality. Atomic Layer Deposition (ALD) might be a good choice to use provided it is possible to deposit Si and SiO₂ at low rate and controllable stoichiometry.

5.2. The Silicon Rich Oxide (SRO) for Si QD

Although there is a large amount of N in these films, the Si content is still high according to XPS result. High temperature annealing was successfully used to form nc-Si in the films, as indicated by the Si XRD peaks in the GIXRD measurements. The intensity of these peaks is relatively low and the nc-Si size evaluated by Debye-Scherrer's equation is only 3nm in average, which is lower than expected.

It seems that the Nitrogen in the film influences the Si crystallization. There should be a high silicon richness to give a higher degree of crystallization. So larger nc-Si could be formed. Dawei Di and et al. [13] who used Si_3N_4 as the barrier layer in the superlattice structure produced by sputtering, reported a similar effect showing that Si crystallization is reduced in thin SRO layers resulting in smaller nc-Si clusters. There is no specific explanation to this issue yet.

Another effect that should be noted is the increase of Si-O content after high temperature annealing. This effect is manifested in the increase of Si-O stretching mode in FT-IR absorbance measurements at 1060cm⁻¹ while, at the same time, the Si-N stretching mode at 860cm⁻¹ decreases. It is not clear whether this is actually due to the transformation of Si-N to Si-O bonds. Although plausible, it is unlikely as breaking the Si-N bonds to form Si-O can hardly happen at the annealing temperature of1100°C.

Another possible explanation for the increase of Si-O bond is that the excess Si is consumed by the unsaturated Si-O bond network. It might also be the reason for low Si crystallization in the films by MW-PECVD. It has been found that the disappearance of Si-H bonds in FTIR comes with a slight increase of Si-O stretching mode if we use 480°C annealing rather than 1100°C. At this temperature, it is less possible to oxidize Si or break the Si-N bonds while it is easy to break the Si-H to induce the formation of Si-O bonds.

This bond transfer effect is common for materials containing H. It has been widely accepted that H in a-Si enhance the low temperature Si crystal formation. H exists in a-Si:H in the form of Si-H-Si. It is easy to break Si-H bonds and release the H making the Si- left behind to form Si-Si bonds [51].

However, there are still questions regarding to the reduction of Si-N bonds as seen by FTIR. What should be pointed out is the disappearance of N-H bonds. It is very interesting to see no increase of Si-N stretching mode due to N-H bonds dissociation. One might conclude that the Si-N bond network might quickly evolve and the Si-N stretching mode will turn to other bond modes connecting to O into an amorphous SiON network.

In order to investigate more in this aspect, XPS might be the best choice to study and identify the actual chemical bonds. It should be possible to identify the Si, N and O covalent status to unveil the chemical bond changes before and after annealing.

Considering the nc-Si formation, there is less knowledge about the understanding of chemical bond change during the nc-Si formation. Further research and literature review should be done in this area.

5.3. Future work for SRO and Si QD

5.3.1. Characterization

There are many other characterization techniques available to evaluate the chemical, optical and electrical properties in the future.

For the chemical properties, XPS could help to give the information of chemical bonds and to diagnose how the bonds change during annealing. TEM will be able to give visual evidence of the formation of Si crystals.

X-Ray Reflectivity (XRR) is not only effective to accurately determine the thickness of thin film in the range from several nm to 200nm, but it can also be

used to evaluate the interface roughness, material inhomogeneity and film density. By fitting the proper model to the experiment data, it allows us to investigate the superlattice structure. With more in-depth analysis it should be possible to not only determine thickness but much more information about the microstructure in the SRO films could be gained.

The electrical properties such as conductivity, surface charges and defect states will be important properties to evaluate the film quality. *I-V* and *C-V* measurement could be applied then.

Photoluminescence (PL) is a very helpful tool to show the photoelectric properties. As the most widely used technique directly showing the quantum effect, PL should be used to test the films fabricated by PECVD to examine the quantum effect.

5.3.2. Device Fabrication

Using the superlattice structure fabricated by PECVD to improve the Si QD device is the final goal. There will be several stages necessary to achieve this in the future.

The very first important stage is to find the parameters used to accurately control the deposition rate. Argon flow rate is the candidate because it has almost no effect on composition and it has only a slight influence on deposition rate. Further increase of the silicon richness is also necessary to obtain larger nc-Si clusters. It is also critical to define the silicon richness for PECVD deposition. The integration of the peak at 99eV binding energy in XPS result is a good indicator of the actual Si richness for films deposited by PECVD.

It will be necessary to investigate the doping of the SRO material and nc-Si (Si QD) to fabricate p-n junction. In this thesis, the doping is not available in MW-PECVD. Therefore, no comparison was made between doped SRO by MW-PECVD and co-sputtering in this thesis.

In theory, In-situ doping and ex-situ doping could be used. However, the insitu doping by PECVD for SRO thin film has not been done before and there

76

is still a question of whether it is possible to attain a high enough dopant concentration in the SRO films.

The ex-situ doping techniques include ion-implantation, diffusion from doping layer and laser assisted doping. These are more promising doping methods to control doping level or doping profile somehow. More importantly, The SRO materials or superlattice materials fabricated by MW-PECVD can be doped with ex-situ methods. So it requires more efforts in future.

Metallization and contact fabrication are also critical. Due to the high intrinsic sheet resistivity, common back contact metallization schemes on the substrate side are not applicable due to the high temperature annealing necessary. To make a vertical contact structure with a back contact on the substrate will require the use of refractory metals such as Mo, W and Ta.

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