

FORMATION OF SILICON NANOCRYSTALS BY LASER PROCESSING OF SILICON RICH OXIDES

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MASTER OF SCIENCE

By

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August, 2012

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in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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M.S. in Physics

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Silicon nanocrystals are well known to exhibit strong luminescence in the visible. Extension of this into a nanocrystal network would be beneficial for many applications. In the light of recent advances on exciton-plasmon interactions and photovoltaic cells, there is renewed interest in the use of nanostructures. Due to quantum confinement, silicon nanoclusters with increased band gaps, are promising for down conversion light and enhanced emission on plasmonic surfaces. Conventional techniques utilize high-temperature processing to obtain the Si-SiO₂ phase separation which uses high thermal budget, not suitable for localized applications not compatible with glass substrates or thin-film stacked structures. An alternative approach capable of avoiding high temperature processing is laser irradiation of substoichiometric amorphous silicon oxides.

In this work, continuous-wave laser processing of Si-rich oxide thin films with varying Si content were performed in order to obtain Si nanocrystals embedded in silica. The role of composition, dwell times and power densities were investigated for Si-SiO₂ phase separation.

We present cw laser processing of PECVD grown and sputtered SiO_x films. XPS, RBS and ERDA techniques were used for the stoichiometry analysis of different composition as grown samples and their optical properties were determined through ellipsometry analysis. Processing was performed with an Ar⁺ laser at 488 nm. The structural changes due to processing were investigated by Raman and photoluminescence spectroscopy. It has been shown that silicon nanocrystals formation depends both on precursor gas composition (hydrogen-diluted SiH₄ and N₂O or CO₂ gases) and on laser power density. PECVD grown hydrogenated SiO_x films were compared with sputtered films with and without hydrogen to identify the role of hydrogen for phase separation.

Keywords: silicon rich oxides, thin film, laser annealing.

ÖZET

SİLİSYUM ZENGİNİ OKSİTLERİN LAZERLE İŞLENMESİYLE SİLİSYUM NANOYAPILARIN OLUŞUMU

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Farklı silisyum oranlarına sahip silisyum zengini ince filmler sönümsüz dalga lazeriyle tavlانarak silika içine gömülü silisyum nanokristaller elde edildi. Kimyasal bileşimin, ısınlama süresinin, ve lazer güç yoğunluğunun Si-SiO₂ faz ayrışmasına olan etkisi incelendi.

Son yıllarda fotovoltatik hücrelerdeki son gelişmelerle birlikte elektromanyetik tayfın daha verimli bir şekilde kullanılması için nanoyapılara olan ilgi de artmıştır. Kuantum hapsolme etkisi sayesinde nanoyapıların bant aralığı artar. Böylece yüksekışığın aşağı çevrimi (Enerjisinin düşürülmesi) mümkün olur. Geleneksel yöntemde Si-SiO₂ faz ayrışması için yüksek sıcaklıkta tavlama işlemi uygulanır. Bu işlemler cam alttaşılar ve seri üretimde kullanılan ince film teknolojisine uygun değildir. Yüksek sıcaklık yöntemine alternatif bir yaklaşım lazerle ısınlamadır.

Bu çalışmada plazma takviyeli kimyasal buharı biriktirme (PECVD) ve saçtırma yöntemleri ile üretilen SiO_x ince filmler sönümsüz dalga lazeriyle tavlانmıştır. Tavlانmamış örneklerin bileşimi x-ışını fotoelektron spektroskopisi(XPS), elastik geri tepme deteksiyonu ERDA, ve Rutherford geri saçılma spektroskopisi (RBS) teknikleri ile, optik özellikleri ise elipsometri analiziyle belirlendi. Tavlama argon iyon lazerinin 488 nm dalgaboyu kullanılarak gerçekleştirildi. Tavlama sonucu oluşan yapısal etki Raman ve fotolüminesans spektroskopisiyle incelendi.

Silisyum nanokristallerin boyut ve miktarının oluşturma gazlarının (Hidrojenle seyreltilmiş SiH₄ ve N₂O ya da CO₂) akış hızına ve lazer güç yoğunluğuna bağlı olduğu gösterildi. Hidrojenin faz ayrışmasındaki rolünü incelemek için

PECVD ve saçtırma ile hazırlanan filmler karşılaştırıldı.

Anahtar sözcükler: Silisyum zengini oksitler, ince film, lazerle tavlama.

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Chapter 1

Introduction

Silicon nanoparticles are of great interest due to their optical properties and potential applications in semiconductor industry. Some of these applications include light emitting diodes [1], non-volatile memories [2], and 3rd generation solar cells [3, 4]. Efficient light emission from silicon nanocrystals makes them a good candidate for silicon based lasers. The indirect band gap of bulk silicon hinders such a possibility. However, when silicon is reduced in dimensionality, its light emitting shows blue shift and emits in the visible. The light intensity is quite large compared to bulk case. Such a source of excitons can be used along with surface plasmons to enhance the emission which may also lead to a Si based plasmonic laser. Studying exciton-plasmon coupling on flat and corrugated metallic surfaces may serve towards this goal.

3rd generation solar cells aim to decrease the cost per produced energy by either increasing the efficiency, or decreasing the cost of production of the cell. Two mechanisms that lowers the efficiency are inability to absorb the photons with energies below the band gap and loss of photonic energy due to thermalisation of the excess carrier energies above band gap. To solve this problem, one strategy is to make multi band gap or tandem solar cells [5, 3]. Due to the confinement effect, silicon nanoparticles have wider band gaps than bulk silicon. This property makes it an ideal material for tandem solar cell. In this design an upper layer of silicon nanoparticles absorb high energy light while the bottom

bulk silicon solar cell absorb the low energy light. Traditional method to obtain silicon nanostructures out of silicon rich oxide is to anneal it in high temperature furnace[2]. However, inserting the whole sample into a high temperature furnace is not suitable for current thin film solar cell technology. We are using an alternative laser irradiation method that locally heats the thin silicon rich oxide film.

Silicon rich oxides are materials that consist of silicon and oxygen with oxygen to silicon ratio lower than 2. Depending on this ratio, excess silicon may aggregate in the form of silicon nanoparticles within silicon dioxide. If this value is close to 1, a silicon sponge-like structure in silicon dioxide is expected [2]. This material consist of a network of nanowires, therefore it is electrically percolated and due to its nanowire structure its energy levels are expected to exhibit quantum confinement phenomena [6].

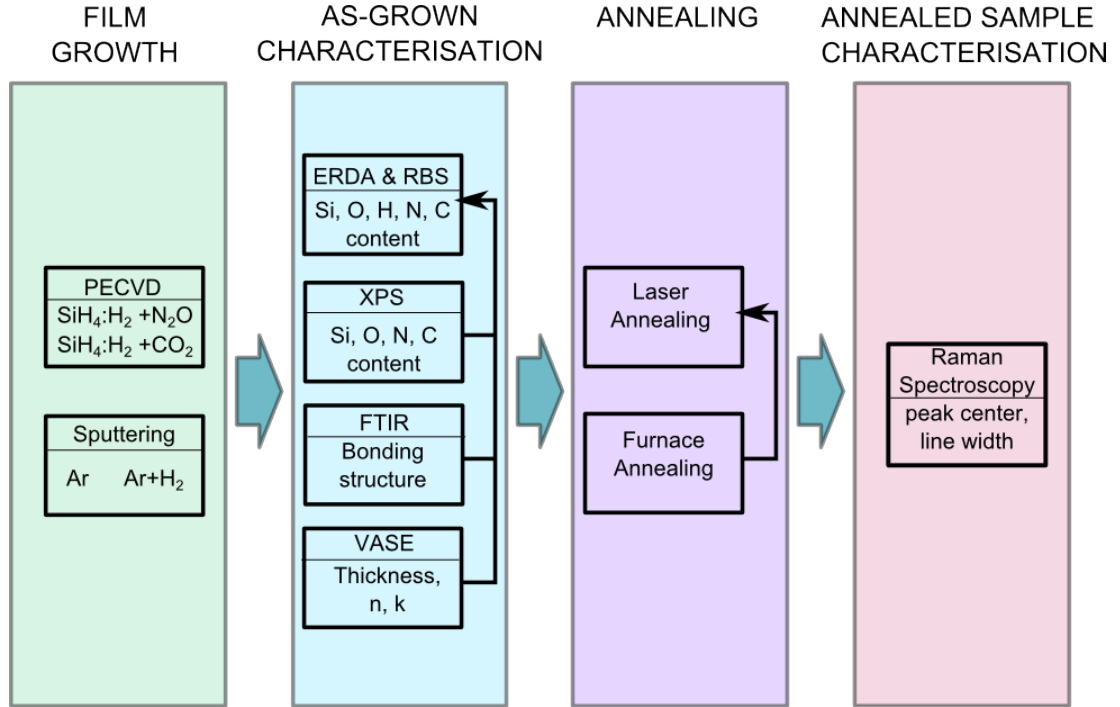


Figure 1.1: Flowchart of this study

Main scope of this work is to analyze the effect of composition of the films and laser power on the nanocrystalline silicon formation which may be used in plasmon-exciton interactions and solar cells. A flowchart is given in figure 1.1. In

this study we deposited silicon rich oxide thin films by Plasma Enhanced Chemical Vapor Deposition (PECVD) and sputter deposition methods. For PECVD, we used 2% silane diluted in hydrogen as silicon source and N_2O or CO_2 as oxygen source. For this reason we expected our films to contain hydrogen, nitrogen and carbon as well as silicon and oxygen. To focus on the effect of hydrogen, we produced two types of sputtered samples: one was sputtered by argon, the other was sputtered by argon mixed with hydrogen. For composition analysis of the as grown films we used Elastic Recoil Detection Analysis (ERDA), X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR). Optical characterisation was done by Variable Angle Spectrometric Ellipsometry (VASE). Laser processing was done in an inverted microscope focusing a 488 nm argon-ion laser beam on the film coated on silicon and fused silica substrates. Laser spot size was between 2-10 μm . Output of the microscope was coupled to a high resolution monochromator, so we could irradiate the samples and obtain the Raman spectra in the same setup. We scanned the samples by a step motor controlled X-Y stage mounted on the microscope during irradiation. We also annealed the samples in a furnace to compare the phase separation temperatures. Crystalline silicon formation was observed and characterised by Raman spectroscopy.

In the next Chapter, we will discuss the motivation and the background of this study and the modeling of the laser heating system by Comsol Multiphysics. Chapter 3 lists the methods used to characterize the unprocessed samples. Chapter 4 explains the laser processing method and the raman characterization of the laser annealed zones as well as the furnace annealed samples. In Chapter 5 we will summarize the results of the characterization and laser processing.

Chapter 2

Background

Silicon rich oxides (SRO) are a type of oxide that has excess silicon. A conventional expression is the SiO_x formulation. When $x=2$ it is considered to be stoichiometric. For silicon rich oxides x is smaller than 2. Due to being non stoichiometric, these oxides tend to separate into two energetically more favorable phases; SiO_2 and Si. This process is dependent on temperature, annealing time, and the number x . Phase separation may follow these steps: nucleation, growth, Ostwald ripening and spinodal decomposition. Nucleation phase is the beginning of the formation of silicon seeds in SRO [7, 8]. These seeds grow by diffusion of more silicon atoms in the growth phase. Ostwald ripening is the merging of the seeds to form larger structures to minimize the surface energy. If the excess silicon is high enough spinodal decomposition occurs. Spinodal decomposition is the separation of the material into two distinct phases (In our case Si and SiO_2) [7, 8, 9, 10, 11]. These two phases are not localized like nucleation, but uniformly distributed forming a sponge-like (or network-like) structure. Phase separation occurs as a result of multiple interactions between atoms including bond breaking, chemical reactions, and diffusional jumps [7, 8]. To break the existing bonds, an activation energy is needed. The activation energy may be supplied by heating the SRO. If kT is in the order of the activation energy, the bonds may break, and if the decomposed state is energetically more favorable, the system reaches to a new equilibrium.

Kinetic Monte Carlo simulations of similar phase separation exists in the literature [7, 2]. Figure 2.1 shows the time evolution of the phase separation. In this study low energy Si+ ions were implanted into SiO₂. (a), (b), and (c) shows different Si+ fluencies ((a) is lowest and (b) is highest). Activation energy is supplied by the kinetic energy of the accelerated ions. At low fluencies the system evolves into Si particles embedded inside SiO₂ (Figure 2.1(a)). At first, nucleation occurs, then gradually these nuclei grow larger. Small nuclei merge to form larger nanoparticles (Ostwald ripening). Higher ion beam fluencies results in larger nuclei (b). Here, the particles that are non-spherical at first evolves into spherical particles. At even higher ion beam fluencies spinodal decomposition occurs and silicon nanoparticles form a kind of network. Finally the system evolve into silicon nanoclusters embedded in SiO₂. Figure 2.2 shows the simulation results((b) and (d)) with scanning transmission electron microscope of actual samples ((a) and (c)). (a) and (b) are low fluence samples and exhibits nucleation (white spots are silicon nanoparticles) while (c) and (d) are high fluence samples that exhibit spinodal decomposition (silicon nanoclusters form a network-like structure). We observe a tendency to form worm-like nanostructures at the higher ion beam fluence. The SEM images are in good correlation with their calculated counterparts.

Spinodal decomposition is particularly interesting due to its sponge-like percolated structure. Percolation gives one the opportunity to manufacture p-n or p-i-n junctions out of p-type and n-type silicon sponges. Another advantage of the sponge-like silicon is its wide band gap. Due to quantum confinement, its band gap is wider than bulk silicon [12]. One of the factors that lowers the solar cell efficiencies is the thermalization of high energy photons. These photons have energies higher than the band gap, therefore the electron excited by one of them would have an energy higher than the conduction band minimum. The excess energy may be converted into phonons causing heating. However, in a tandem configuration (e. g. a silicon solar cell coated with p-n junction of sponge-like silicon) high energy photons may be absorbed by sponge-like silicon and low energy photons by silicon solar cell for efficient use of solar spectrum and reducing heating due to thermalization.

Sponge-like silicon also has potential to enhance the absorption of light due to its textured structure. In our case it is also embedded in SiO_2 which provides passivation by reducing dangling bonds. These dangling bonds cause intermediate states between the band gap and the conduction band. Electrons and holes produced by the absorbed light may recombine easily over these intermediate states. For silicon, oxidation removes these states, therefore surface of the silicon is passivated by oxygen or sulphur. Due to being embedded into silicon dioxide as a whole, silicon nanostructures produced by our method have an effective passivation [13].

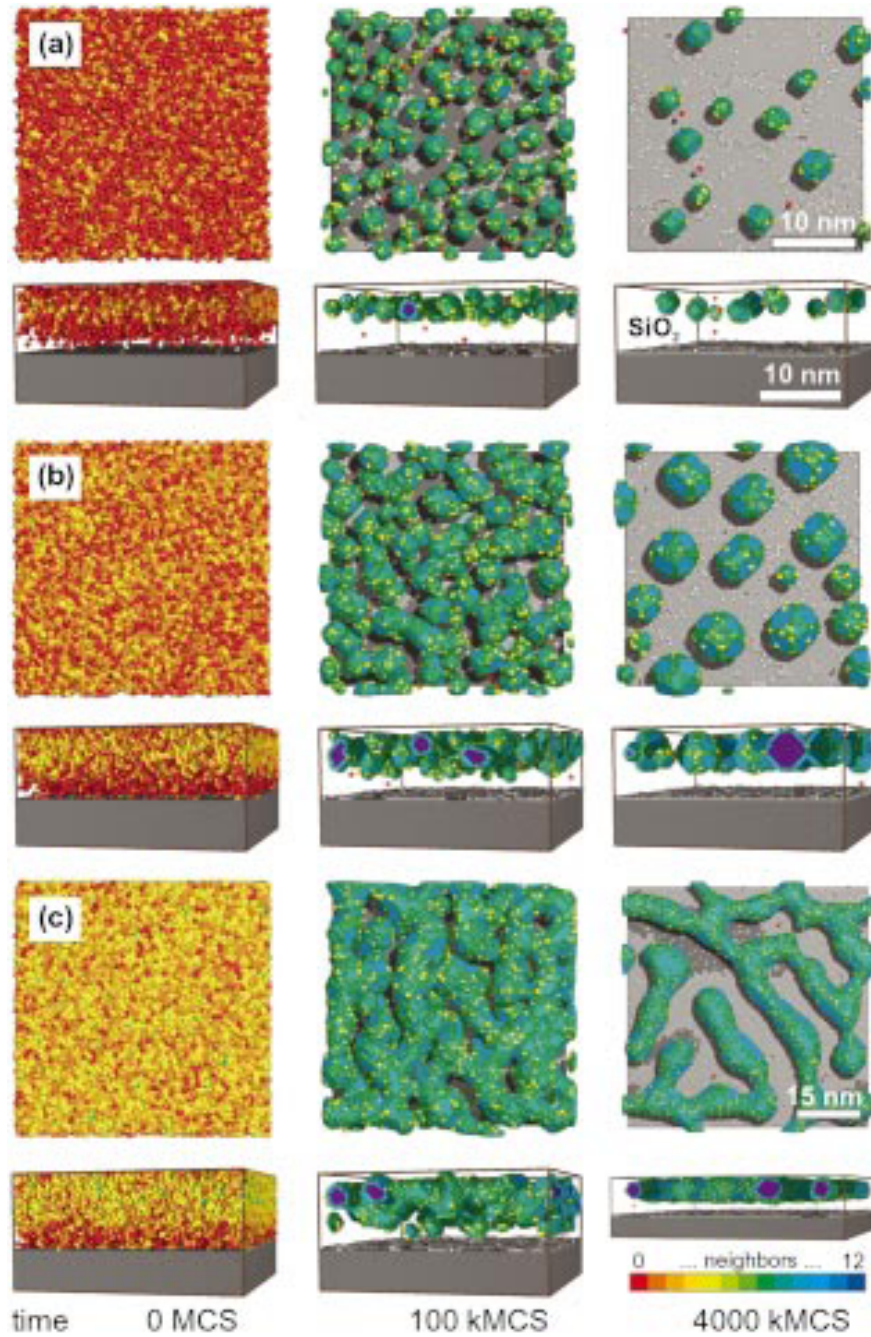


Figure 2.1: Kinetic Monte Carlo calculations of low energy Si^+ ion implantation into SiO_2 .

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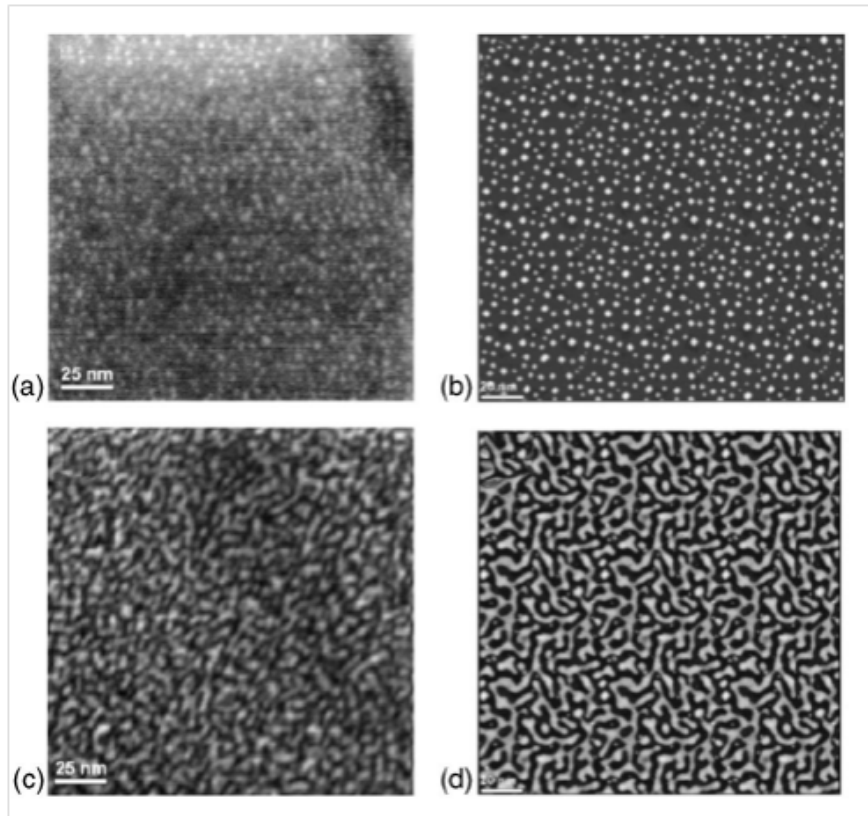


Figure 2.2: STEM images ((a) and (b)) and Kinetic Monte Carlo calculations ((c) and (d)) of ion implanted samples.

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2.1 Heat Transfer Simulation

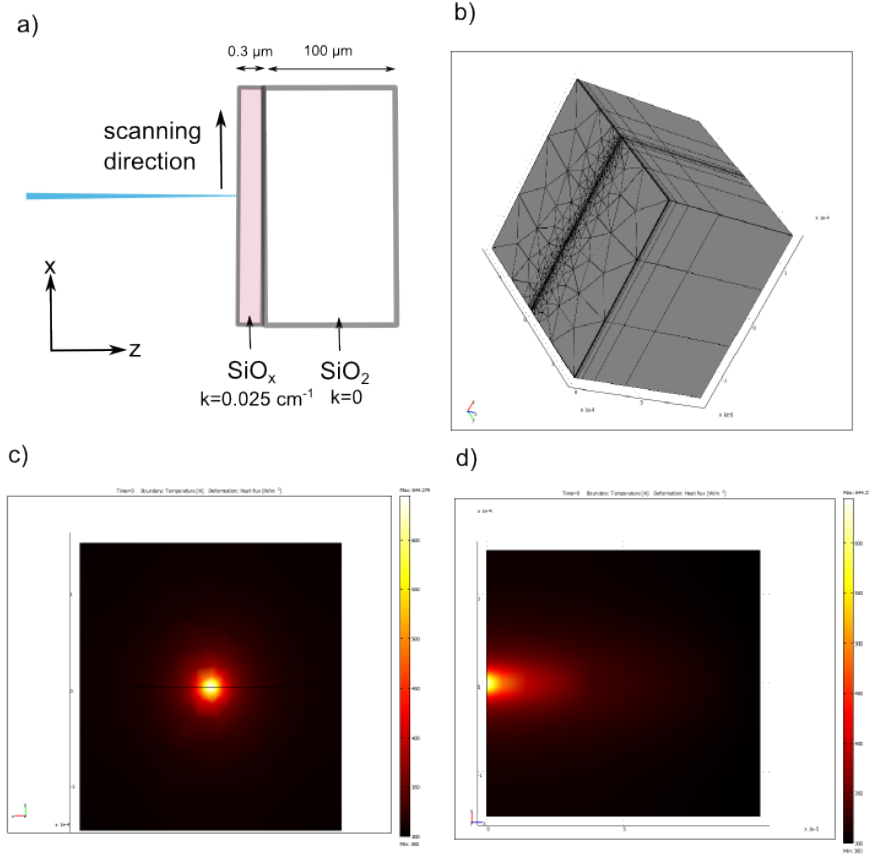


Figure 2.3: Schematics of numerical simulation of temperature rise during laser irradiation. (a) Scan geometry, (b) Finite element discretization (c) laser spot (top), (d) laser spot (sideways)

Annealing temperature plays an important role on formation of silicon nanoparticle formation in SRO. In the case of furnace annealing, temperature can be measured easily, yet it is a difficult task to measure the temperature on the laser processed zones during the process. It is possible to calculate the temperature that the film reach approximately, given the laser power, laser spot size, and optical and thermal properties of the sample. In this section, calculation of heating of silicon rich oxide thin film on a silica substrate by a laser is explained.

We simulated the heating of a film coated sample by a moving laser beam by Comsol Multiphysics Conductive Heat Transfer Module. Using finite element

method, this software solves the heat transfer equation:

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = Q$$

where C_p is the specific heat capacity, ρ is the density, k is the Boltzmann constant and Q is the heat source term. In our case, the laser beam is absorbed by the film and the intensity of the laser decays exponentially into the film. Heating occurs via absorption of light. Therefore, we have to add the laser beam as a heat source into the equation. To do this we have to calculate how much light is absorbed by the film. Assuming absorption is constant (i. e. not dependent on temperature or light intensity) laser intensity obeys Beer-Lambert law:

$$I(z) = I_0 e^{-\alpha z}$$

where I_0 is the initial power density and α is the absorption coefficient. Absorption coefficient depends on the wavelength of the light, λ , as well as the complex component of the refractive index k :

$$\alpha = \frac{4\pi k}{\lambda}$$

Initial power density also varies spatially, assuming our laser has a Gaussian beam profile, I_0 should be:

$$I_0(x, y) = \frac{I_{total}}{\sigma\pi} e^{-(x^2+y^2)/\sigma^2}$$

It is normalized so that the total initial power is I_{total} . σ is the beamwidth. If the beam is moving in the x direction the intensity should be time dependent.

$$I_0(x, y, t) = \frac{I_{total}}{\sigma\pi} e^{-((x-vt)^2+y^2)/\sigma^2}$$

Inserting the intensity we found into Beer Lambert law we find that the heat source term due to the laser absorption should be:

$$Q = 4k I_{total} e^{-(4\pi k z)/\lambda} e^{-(x-vt)^2+y^2)/\sigma^2)/(\lambda b^2)}$$

Comsol Multiphysics uses finite element method to solve the heat transfer equation. It divides the given structure into discrete parts called a polygon mesh. Therefore it reduces the continuous equation into finite number of elements. The

more the number of these pieces, the better the precision. However, high number of element cause long calculation time. To solve this, a common technique is to make the mesh denser in the point of interest and sparse in other places. In our case, the point of interest is the line that the focused laser beam moves over.

Parameter	Value
Laser power	100 mW
Scan speed	0
Beamwidth	80 μm
Extinction coefficient	0.025 cm^{-1}
Wavelength	488 nm
Film thickness	300 nm
emissivity 6	0.92

Table 2.1: Parameters used in Comsol simulation.

The structure simulated is shown in figure 2.3(a). In figure 2.3(b) how the mesh density varies on the structure is shown. It gets denser on the scanned line and the film surface. We have defined the film thickness to be 300 nm and the substrate to be 100 μm . Our actual substrates is around 1mm thick, but we saw that temperature drops to almost 300 K after 80 μm . The extinction coefficient k is measured by ellipsometry for our films and it was assumed to be zero for SiO_2 substrate. Temperature dependent thermal conductivity and heat capacity was selected as SiO_2 for both the film and the substrate. To understand the time dependence of the temperature we calculated a beam that is suddenly turned on but not moving on the sample. The parameters are given in Table 2.1. We calculated the time dependence of the temperature at the center of the beam with varying beamwidth and the laser power. In figure 2.5 different incident powers, in figure 2.4 different beamwidths are shown while all other parameters are kept as in table 2.1. We see that the system reaches to an equilibrium temperature after about 100 μs . Our experimental scan speeds are between 50 $\mu\text{m/s}$ and 1000 $\mu\text{m/s}$ so the corresponding dwell times for 10 μm beamwidth are 0.2 s and 0.01 s. We therefore expect the scan speed dependence of the induced maximum temperature during the scan to be negligible for this range of dwell times. However, scan speed determines the dwell time and the

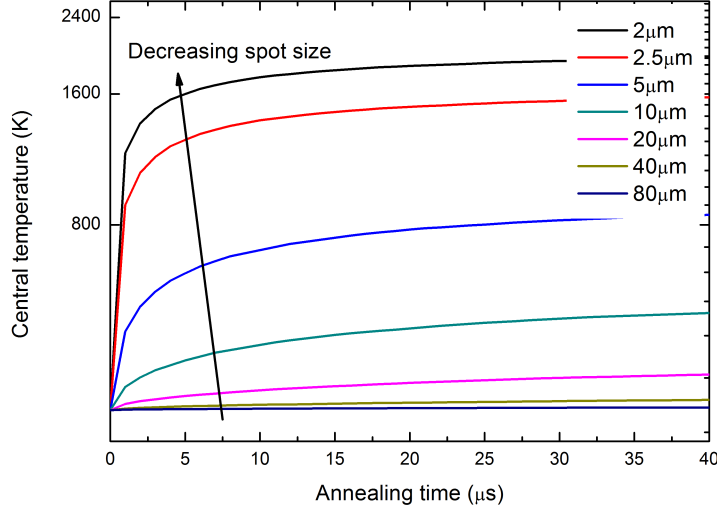


Figure 2.4: Temperature at the laser spot center as a function of annealing time for different beamwidths. Laser power is 100mW.

crystallization ratio, as we will see in the 4th chapter. Figure 2.6 shows the equilibrium temperature when the beamwidth is constant. A linear relationship between the temperature and the beamwidth is observed. Figure 2.7 shows the equilibrium temperature of the center when the beamwidth is varied but total power is held constant. Same amount of total heat diffused faster when it is confined in a smaller space, due to the higher temperature difference between the heated zone and the environment. This explains the exponential decay form in figure 2.7. Figure 2.3(c) shows the temperature plot from the top view (in the z direction). Temperature is maximum at the center and the heat radially dissipates to the film. Figure 2.3(d) is the temperature plot in the cross section view, heat penetrates into the substrate by 10-20 μm (full width at half maximum of temperature).

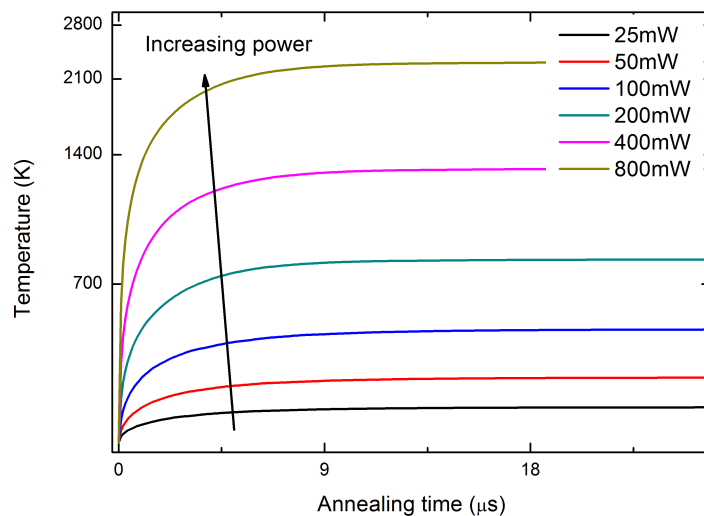


Figure 2.5: Temperature at the laser spot center as a function of annealing time for different laser powers. Beamwidth is 10 microns.

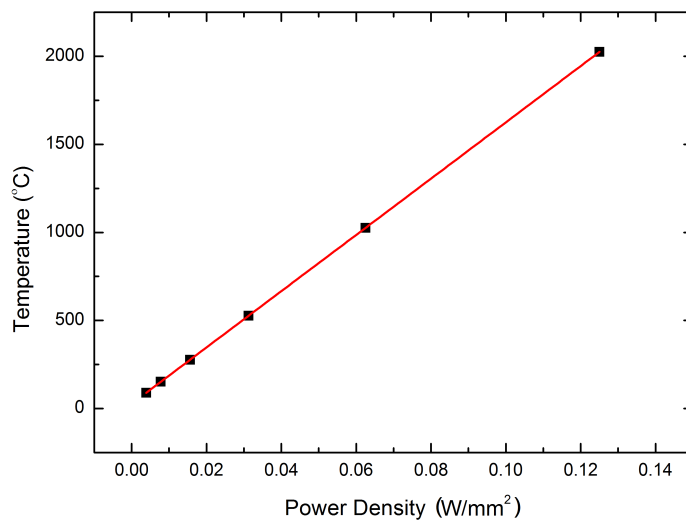


Figure 2.6: Equilibrium temperature at the laser spot center as a function of power density. Laser power is 100 mW.

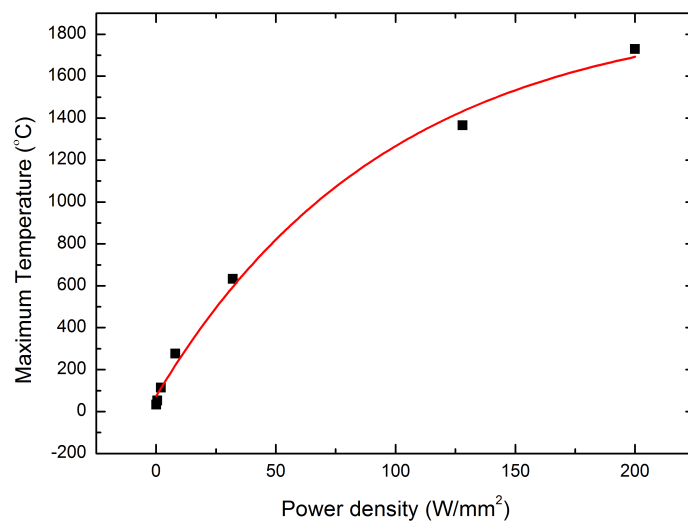


Figure 2.7: Equilibrium temperature at the laser spot center as a function of power density. Laser beamwidth is $20\text{ }\mu\text{m}$.

2.2 Conclusion

In this chapter we have explained the mechanism of silicon nanocluster formation in a silicon rich oxide. Excess silicon forms nanoclusters inside silicon dioxide via nucleation, Ostwald ripening and spinodal decomposition. For nanocrystal formation, an activation energy is needed and this energy is supplied by heating. A possible way of heating is laser processing. Laser light is absorbed by the film producing heat. The heat dissipates according to the heat transfer equation. We have explained a method for simulation of such a system by Comsol Multiphysics. We found that the maximum temperature depends on the spot size and laser power. The Comsol study gives us rough guidelines and trends for induced temperatures as a function of laser power and spot size. As we do not know the exact temperature induced during the experiment it is not possible to compare the results of the Comsol study with experiment on an absolute scale. A tutorial for Comsol Multiphysics is supplied in Appendix A. Similar systems can be modeled by the method explained here. In the next chapter, we will explain the thin film growth methods by PECVD and sputter deposition and characterisation of the as-grown samples by ERDA, XPS, FTIR and ellipsometry.

Chapter 3

Sample Preparation and As-Grown Characterisation

We prepared 5 groups of samples by the following methods:

1. PECVD with $\text{SiH}_4:\text{H}_2$ and N_2O
2. PECVD with $\text{SiH}_4:\text{N}_2$ and N_2O
3. PECVD with $\text{SiH}_4:\text{H}_2$ and CO_2
4. Sputtering SiO_2 with Argon
5. Sputtering SiO_2 with Argon and Hydrogen

In this section we will explain PECVD and sputtering methods and analysis of as-grown films by ERDA, XPS, FTIR and ellipsometry.

3.1 Sample preparation

3.1.1 Preparation of SiO_x by PECVD

Plasma Enhanced Chemical Vapor Deposition (PECVD) is a method for manufacturing thin films at relatively low temperatures. A schematic is shown in figure 3.1. A gas mixture flows into a chamber which is vacuumed constantly by a mechanical pump and a root pump. Flow rates of the gases are adjusted by mass flow controllers. The pressure inside the chamber is controlled by an adaptive pressure controller. This pressure controller is an adjustable valve that moves in accordance with the pressure inside the chamber to keep the pressure constant. Pressure is generally of the order of 1 Torr. This low pressure gas is ionised by an RF antenna which produces radio waves at 13.56 MHz. Reactive ions deposit on the sample. Thickness of the film is proportional to the growth time. It is possible to heat the substrate to provide surface mobility for adsorbed ions. The chamber is vacuumed to a pressure of 10^{-5} Torr by a turbomolecular pump to evacuate air prior to the operation. Substrates are cleaned by an oxygen plasma to remove possible organic contaminants before coating.

The films were deposited in two different radial flow capacitively coupled parallel-plate PECVD reactors. For both reactors chamber pressure was fixed at 500 mTorr and substrate temperature at 250°C . Deposition time was set separately to obtain film thicknesses of 300 or 500 nm. For each film, fused silica, boron doped p-type silicon and infrared transparent silicon substrates were used. Table 3.1 lists the the films grown with flow rates of the gases used. Two mixtures of silane were used. The first is 2% silane in H_2 and the second is 2% silane in N_2 . H and N series were grown in the same reactor while C series were grown in another reactor which has a CO_2 tank connected.

Sample Code	Flow Rate (sccm)			
	2% SiH ₄ in H ₂	2% SiH ₄ in N ₂	N ₂ O	CO ₂
H1	500	-	3	-
H2	500	-	5	-
H3	500	-	6	-
H4	500	-	7	-
H5	500	-	8	-
H6	500	-	9	-
H7	500	-	10	-
H8	500	-	13.5	-
H9	500	-	20	-
H10	500	-	40	-
N1	-	500	3	-
N2	-	500	7	-
N3	-	500	9	-
N4	-	500	10	-
N5	-	500	13.5	-
N6	-	500	20	-
C1	350	-	-	10
C2	350	-	-	20
C3	350	-	-	30
C4	350	-	-	40
C5	350	-	-	50

Table 3.1: List of samples prepared by PECVD.

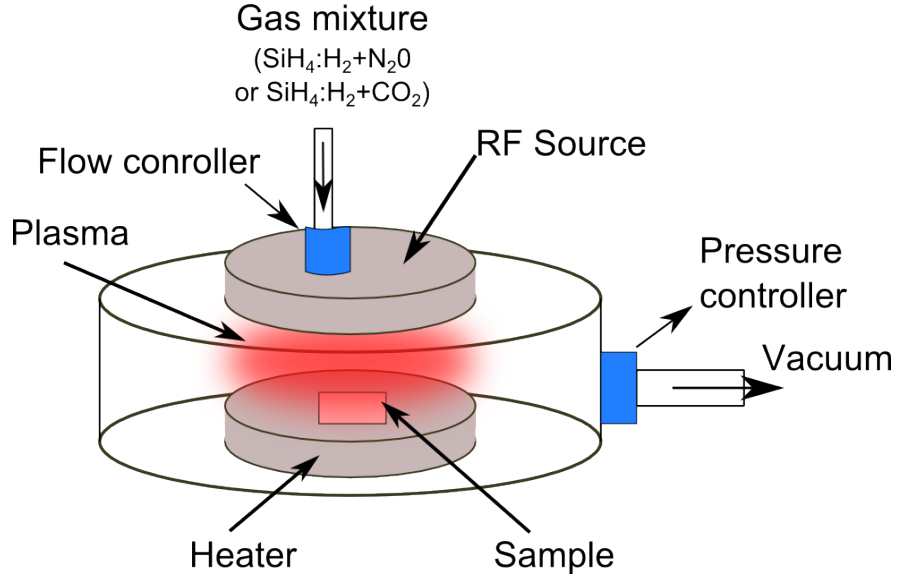


Figure 3.1: Schematic of the PECVD reactor.

3.1.2 Preparation of SiO_x by sputtering

Sputtering is a physical vapor deposition method for manufacturing thin films. Its principle of operation is shown in figure 3.2. Argon gas flows into the growth chamber and ionized by the RF forming Ar^+ ions. These ions are accelerated under the same electric field hitting the target. Some atoms are removed from the target by the impact. These are the sputtered atoms and a part of them condense on the sample. In some cases, sample holder is rotated to obtain a more uniform film. To make silicon rich oxide thin films silicon and silicon dioxide targets were used, simultaneously. For insulating targets, DC voltage may cause charge buildup, for this reason RF voltage was used to sputter SiO_2 target. Sputtering parameters are given in table 3.2.

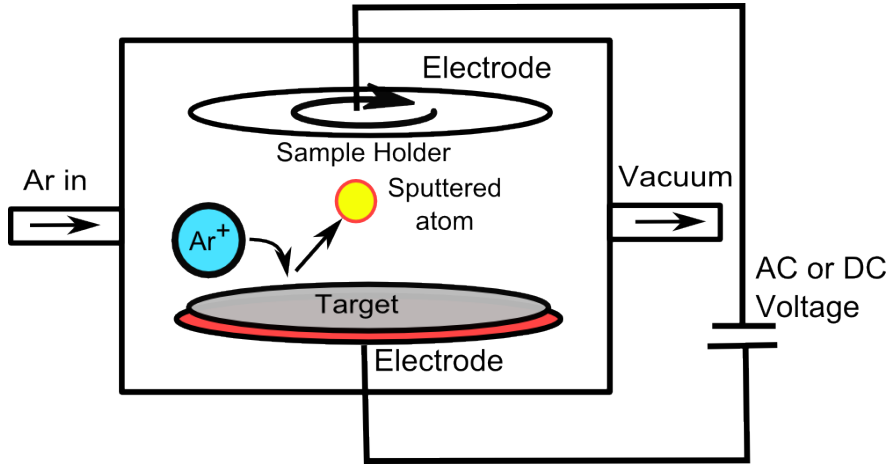


Figure 3.2: Schematic of the sputter deposition system.

Base pressure	4.5×10^{-6} Torr
Working pressure	4 mBar
Process gases	Ar 20 sccm H ₂ 4 sccm
Process temperature	Room temperature
Time	1 hour
Power (Si)	54 W DC
Power (SiO ₂)	180 W RF
Film thickness	250 nm

Table 3.2: Sputtering parameters

3.2 Characterisation of as-grown samples

3.2.1 Composition Analysis by ERDA

Determination of composition is critical for our samples since formation of nanocrystal depends on the ratio of silicon to oxygen as well as nitrogen and hydrogen content. Composition also affects the temperature threshold for nanocrystalline formation as we will discuss in the next chapter. PECVD grown films contain H,N and C as well as Si and O making the compositional analysis difficult. Measuring the hydrogen content in these films is particularly difficult. This is the main reason of requirement for ERDA. In this section we will discuss the ERDA measurements and results.

Elastic Recoil Detection (ERD) is an ion-beam technique which allows the quantitative, compositional depth-profiling of thin films containing light elements. The strengths of this technique include its ability to combine unambiguous element identification, with depth profiling and a direct quantitative result. This is especially one of the most sensitive methods for the detection of hydrogen, and, in that sense, an essential technique in our study, since our samples contain H due to SiH_4 and H_2 which used as a balance gas to SiH_4 .

The ERD measurements were performed using 35 MeV Cl^+ ion beam at Helmholtz Zentrum Dresden-Rossendorf, Germany. The ion beam is incident on the sample at a given angle and the scattered particles are collected by a detector sensitive to the energy of the recoiling ions. Because the amount of energy transferred to the sample atom depends on the ratio of masses between the ion and the sample atom, the chemical composition of the sample can be determined from measuring the energy of scattered elements. The angle between the sample normal and the incoming beam was 75° and the scattering angle 31° . A Bragg ionization chamber was used to observe the recoiling ions. This chamber has a full energy detection circuit to obtain ion energies as well as a fast timing circuit to obtain a Z dependent signal to separate ion species. Recoiled H-ions were

detected within a separate solid state detector at a scattering angle of 41° , preceded by a Mylar foil to stop other scattered and recoiled ions. All spectra were recorded for the same number of incident projectile ions.

The principle of the analysis consist in the fact that the areal density N_i for the element (i) can be determined from the detector solid angle Ω , the integrated peak count A_i for Q incident ions, and the cross section $\sigma_i(E, \theta)$ by the equation:

$$N_i = \frac{A_i \cos \theta}{Q \Omega \sigma_i(E, \theta)}$$

There are two approaches for the analysis of ERDA data, the first one is the spectral scaling approach which consists of using interpolation of tabulated recoil cross-sections and effective stopping powers to determine the scaling factor for each channel, then the energy scale is transformed to depth and the counts converted to concentration [14]. The second approach is the spectral simulation where some theoretical approximations can lead to relatively fast calculations taking into account the mass of the target nuclei and the depth of the target nuclei [15]. The data in this study were fitted using the NDF simulation program [16].

Typical energy spectra for different elements are displayed in Figure 3.3. X-axis (Channels) indicates the energy of the recoiled ions while y-axis indicates the number of ions detected at that energy. Each plot shows the energy distribution of an element. Red lines indicate the theoretical results calculated by simulations which were fitted to the experimental data.

Simulated energy spectra of the expected atoms are fitted to experimental spectra. From the intensities of the fitted spectra, atomic percentages are extracted. Figures 3.4, 3.5, and 3.6 shows the ERDA results for compositional analysis of our samples. As expected, oxygen content is proportional to flow rates of N_2O and CO_2 gases. For all series hydrogen flow rate is fixed and ERDA shows that hydrogen content is relatively constant, compared to silicon and oxygen contents. For N series, nitrogen mostly comes from the silane mixture (as well as smaller amount of N_2O), therefore almost constant, which is consistent with the ERDA results. A small amount of carbon (1-2 percent) was found in H

series which may be due to atmospheric contamination. 2-3 percent carbon exists in C series, but it does not seem to be proportional to the CO₂ flow. According to the ERDA data, in all off the series, hydrogen content seems to decrease slightly with N₂O or CO₂ flow.

Table 3.3 lists the results of the ERDA analysis for all series. The first column is the sample codes with flow rates. The second column is the measured atomic density (atoms/cm²). The next 5 columns are atomic percentages of element Si, O, N, H, C. The last column is the ratio of the sum of oxygen and nitrogen content to the silicon content. For C series and sputtered samples carbon content is also included. To obtain sponge-like silicon nanoclusters after annealing, Si/(O+N) ratio is expected to be close to 1. From the table, the ratio should be 1 between H7 and H8 for H series, between N4 and N5 for N series, and between C4 and C5 for C series.

Atomic sensitivity of ERDA rapidly decreases as the mass of the element increases. This may be compensated by the abundance of the said element in the film to some degree. If the number of counts is low and the data is noisy (See figure 3.3(d)) than error propagates to elemental ratios of film contents making the correlation between different analytical techniques not reliable. This method is sensitive to light elements like hydrogen and not to heavy elements such as silicon, nitrogen and oxygen, as indicated by the higher noise/signal ratio. In our case, silicon concentration is very large, the determination of ERDA for silicon is reliable.

Since ERDA is a sophisticated and expensive technique requiring expensive technical equipment and hard to reach, we seek alternative approaches for composition analysis such as XPS and FTIR. These methods will be examined in the next sections.

SiH ₄ :H ₂ / N ₂ O	Density at./cm ²	Si (%)	O (%)	N (%)	H (%)	C (.%)	(O+N) /Si
H1 (500/3)	2380*10 ¹⁵	63	18	3.2	13	3.4	0.34
H2 (500/5)	2380*10 ¹⁵	60	23	4.2	11	1.8	0.45
H3 (500/6)	4500*10 ¹⁵	56	26	4.4	12	1.8	0.54
H4 (500/7)	2760*10 ¹⁵	56	26	5.2	11	1.9	0.56
H5 (500/8)	3170*10 ¹⁵	54	26	5.9	11	2	0.59
H6 (500/9)	2600*10 ¹⁵	52	29	5.8	11	1.9	0.67
H7 (500/10)	3280*10 ¹⁵	51	31	6.1	11	1.6	0.73
H8 (500/13.5)	2040*10 ¹⁵	40	39	9.2	12	0	1.21
H9 (500/20)	2540*10 ¹⁵	38	39	11	13	0	1.32
H10 (500/40)	3100*10 ¹⁵	33	42	12	13	0	1.64
SiH ₄ :N ₂ / N ₂ O	Density at./cm ²	Si (%)	O (%)	N (%)	H (%)	C (.%)	(O+N) /Si
N1 500/3	2355*10 ¹⁵	47.8	12.4	19.2	20.4	0	0.66
N2 500/7	1717*10 ¹⁵	47	22	16	16	0	0.81
N3 500/9	1667*10 ¹⁵	49	18	17	17	0	0.71
N4 500/10	1336*10 ¹⁵	44	23	17	16	0	0.91
N5 500/13.5	1310*10 ¹⁵	38	34	17	11	0	1.34
N6 500/20	710x10 ¹⁵	34	38	17	11	0	1.62
SiH ₄ :H ₂ / CO ₂	Density at./cm ²	Si (%)	O (%)	N (%)	H (%)	C (.%)	(O+N +C) /Si
C1 350/10	1309*10 ¹⁵	55	26	2.1	14	3.5	0.57
C3 350/30	1210*10 ¹⁵	48	38	1.8	8.4	3.8	0.91
C4 350/40	1200*10 ¹⁵	45	42	1.1	7.8	4.1	1.05
C5 350/50	1170*10 ¹⁵	44	43	1.3	7.8	4.1	1.10
Sputter	Density	Si (%)	O (%)	N (%)	H (%)	C (.%)	(O+N +C) /Si
Ar only	1980*10 ¹⁵	45	48	1.2	3.2	1.9	1.14
Ar + H ₂	1380*10 ¹⁵	46	46	1.3	5.2	1.4	1.06

Table 3.3: Compositional analysis of all samples using ERDA

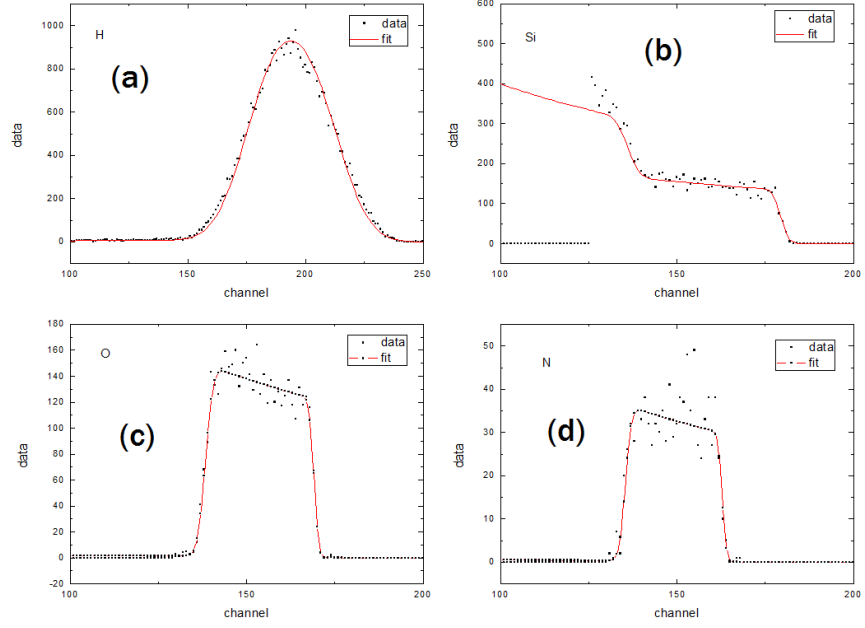


Figure 3.3: ERDA spectra and simulation (red lines) data for H8 film for hydrogen(a), silicon(b), oxygen(c) and nitrogen(d) elements

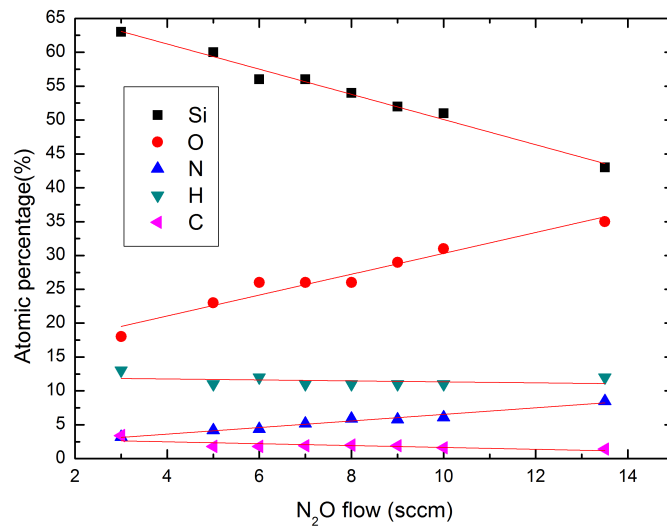


Figure 3.4: Atomic percentages extracted from ERDA data for H series.

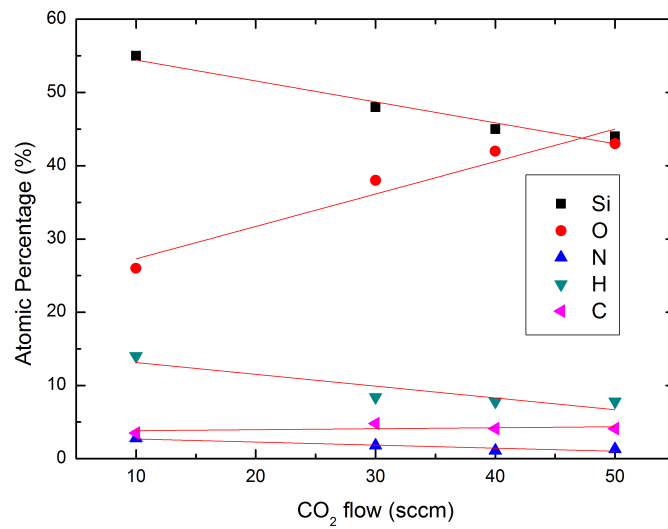


Figure 3.5: Atomic percentages extracted from ERDA data for C series.

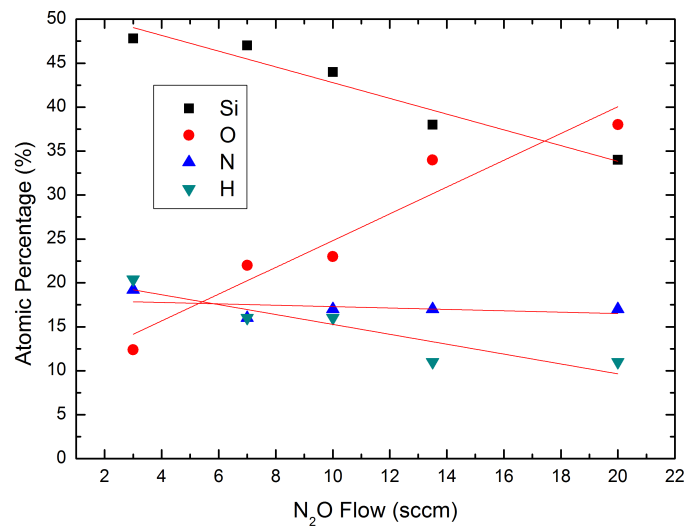


Figure 3.6: Atomic percentages extracted from ERDA data for N series.

3.2.2 Composition analysis by XPS

X-ray photoelectron spectroscopy (XPS) is another method for compositional analysis of thin films. In this method, thin film is irradiated by a focused x-ray beam causing photoemission of electrons (Figure 3.7). The emitted electrons are collected by an energy sensitive detector and their binding energy that depends on the type of the atom and its chemical state, can be determined using the following equation:

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi)$$

where $E_{binding}$ is the binding energy of the electron, E_{photon} is the energy of the X-ray photons being used, $E_{kinetic}$ is the kinetic energy of the electron as measured by the instrument and ϕ is the work function of the spectrometer. Energy of the emitted electrons is dependent on both the energy of the incident x-ray and the binding energy of electron to the atom. Binding energy depends on the type of atom and its chemical state. Therefore analysis of the energy spectrum yields the elemental concentration and their chemical state information. Photoemitted electrons come from the top 1 to 10 nm of the material analyzed. XPS is then a surface chemical analysis technique. To acquire information from the depth of the sample, during the analysis an argon ion beam is sent to the analyzed zone to obtain depth profile (Figure 3.8). Unlike ERDA, XPS is not sensitive to hydrogen content. ERDA analysis shows that the films contain a substantial amount of hydrogen, therefore atomic concentration results from XPS should be calibrated according to ERDA results.

XPS spectra were acquired in Koç University, with a Thermo Scientific K-alpha monochromatic XPS with Al anode. Snap mode acquisition with pass energy of 150 eV was used. The spectra were energy deconvoluted to increase resolution before data processing. Flood gun was used for charge compensation, the base pressure was about 2×10^{-9} Torr, and experiments were performed under a vacuum of 2×10^{-7} Torr. For the depth profiling of the samples, the thin film surfaces were etch by 1000 eV Ar^+ ions. The estimated Ta_2O_5 benchmark etch rate under these conditions was 0.50 nm/s. The etching was done azimuthal rotation to ensure homogenous etching, the etch duration was 10 s with 200

cycles or more. Figure 3.9 is the analysis of energy spectra of C, N, O and Si for the sample H7. X axis shows the calculated binding energies, while Y axis shows the number of electrons counted at that energy. O 1s, N 1s, C 1s and Si 2p photoemission peaks were recorded and the binding data were referenced to the aliphatic carbon line at 284.5 eV. The Si 2p peak was deconvoluted into different Si^{n+} species. C 1s peak also shows two peaks at 285 and 287 eV corresponding to C^0 and C^+ . Peak areas were used, with the appropriate sensitivity factors, to determine the composition of the material. The analysis was done using the Cofield library (for Al source) from Thermo Scientific.

Since the films contained hydrogen and XPS cannot detect hydrogen, atomic concentrations may not be determined directly. However, ratios of detectable elements like silicon, oxygen and nitrogen may yield reasonable values. Figure 3.10, 3.11, 3.12 and 3.13 shows the correlation of XPS and ERDA compositional analysis for the films grown. In the figures X axis is the N/Si or O/Si ratio from XPS and Y axis is the same ratio from ERDA. A linear fit with slope close to 1 indicates that O/Si ratio from XPS and ERDA is close, therefore it may be possible to measure the ratio of oxygen atoms to silicon atoms directly by XPS. For the case of N/Si ratio, H series have a positive correlation, but N series, that has the highest nitrogen content, have a negative correlation. C series, that have low nitrogen content, exhibit a positive correlation between ERDA and XPS data, but has a large margin of error due to the low N content. Also ERDA is less sensitive to heavier elements, nitrogen is heavy and its amount in the films is low, therefore N content from ERDA data is noisy (See figure 3.3(d)). The relationship between ERDA and XPS for N/Si ratio may depend on overall N content of the film, but can be better calibrated by analyzing more data to improve signal to noise ratio. Therefore O/Si and N/Si ratios may be measured by XPS, and if the hydrogen content is known, atomic concentrations may be calculated as well. FTIR is sensitive to hydrogen, and may provide clues on hydrogen content of the films; this will be discussed in the next section.

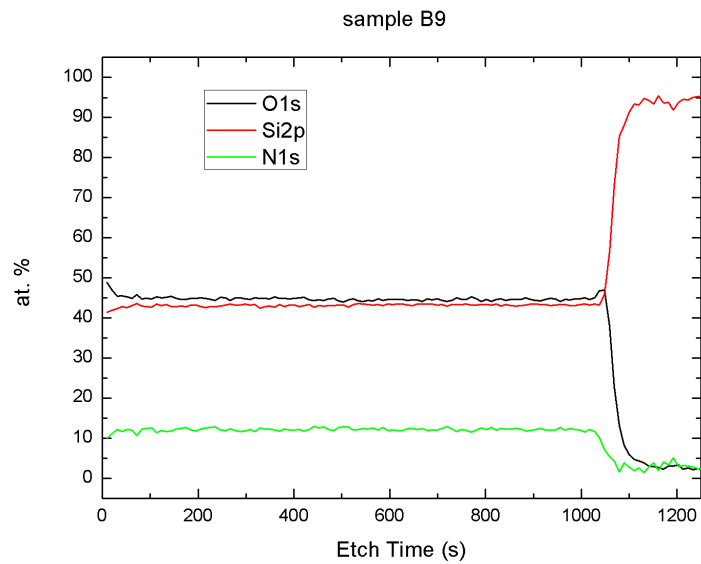


Figure 3.8: XPS depth profile. Y axis is the atomic concentrations. X-axis represents the etched depth of the sample.

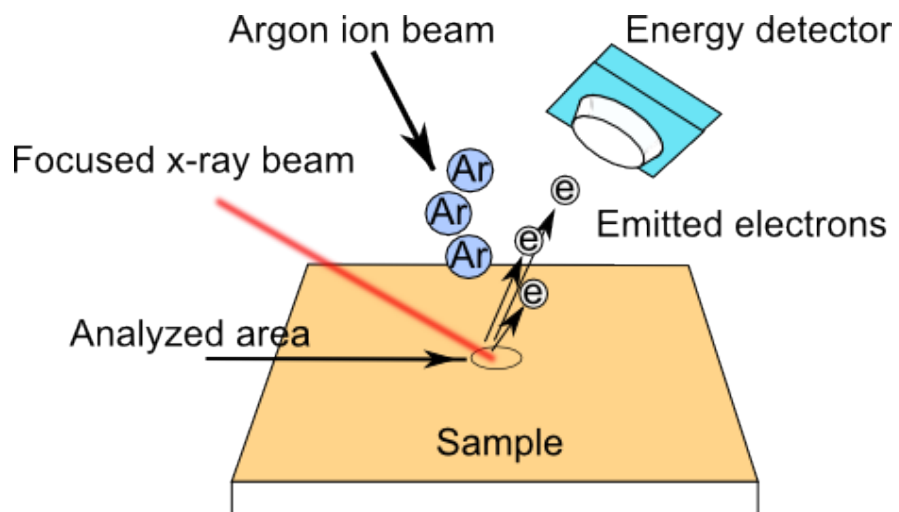


Figure 3.7: Schematic explanation of XPS.

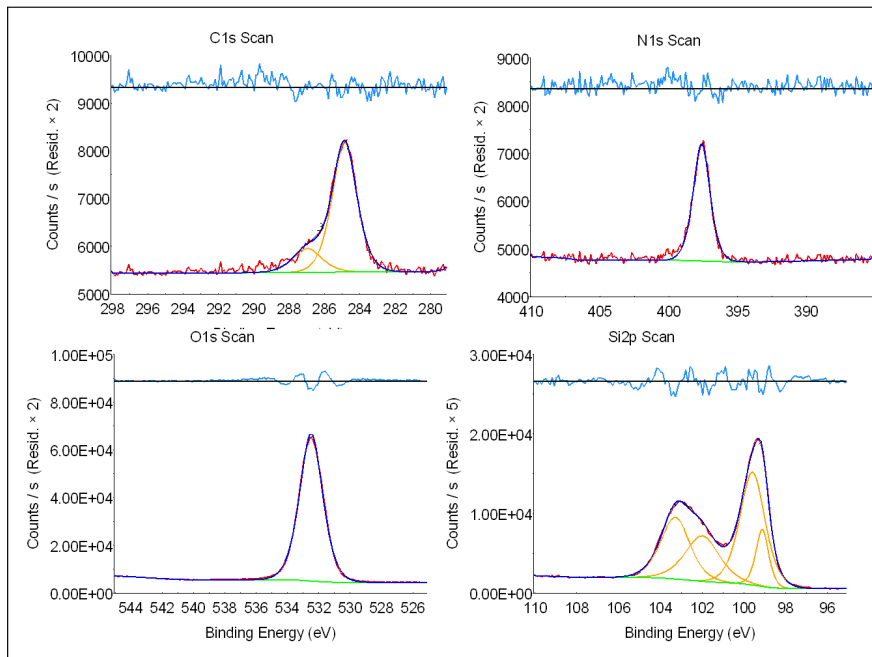


Figure 3.9: Example XPS spectrum. The graphs show clockwise, C 1s, N 1s, Si 2p and O 1s peaks, respectively.

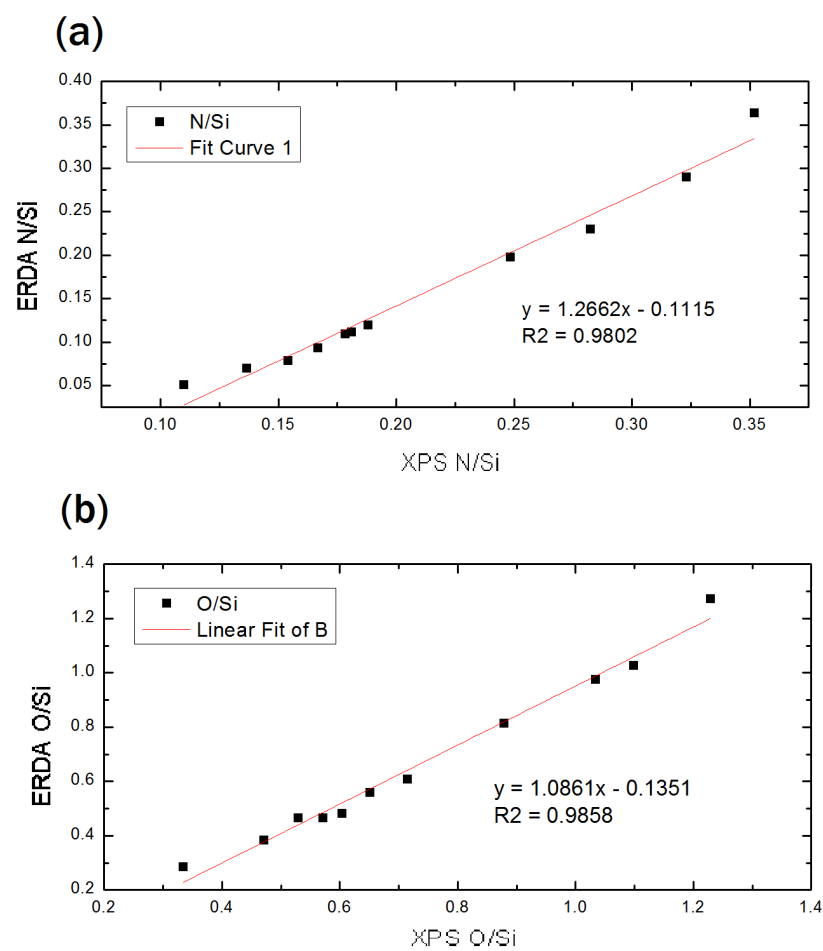


Figure 3.10: Atomic percentage ratios extracted from XPS compared to ERDA data for H series. (a) N/Si ratio, (b) O/Si ratio.

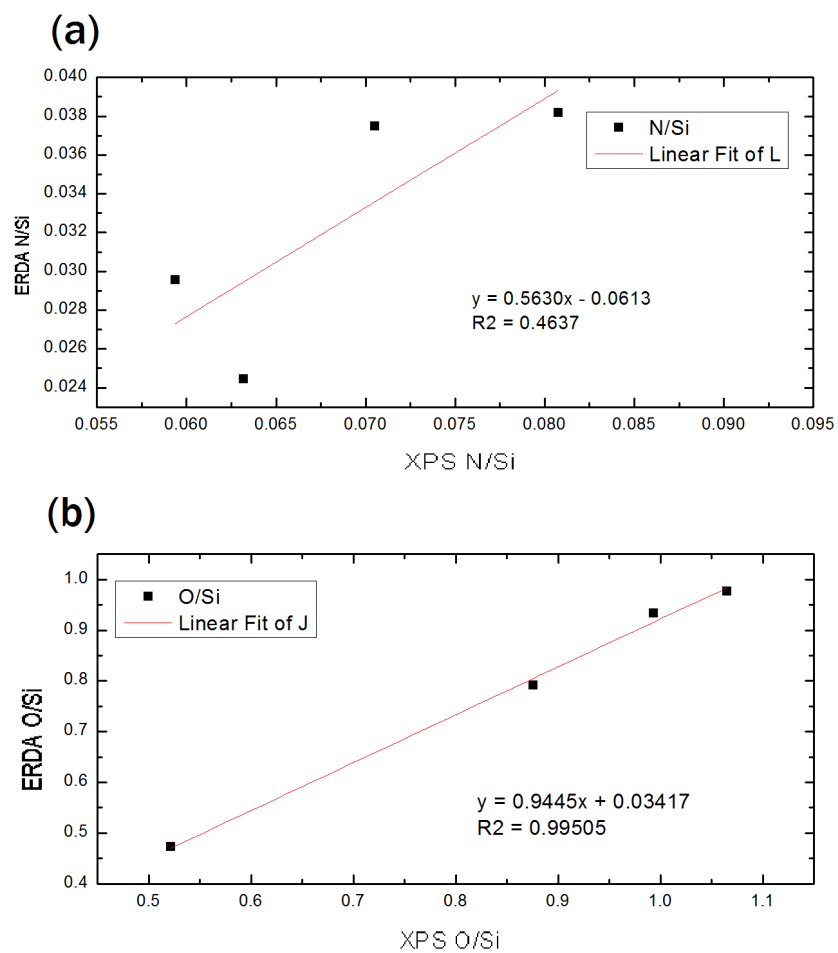


Figure 3.11: Atomic percentage ratios extracted from XPS compared to ERDA data for C series. (a) N/Si ratio, (b) O/Si ratio.

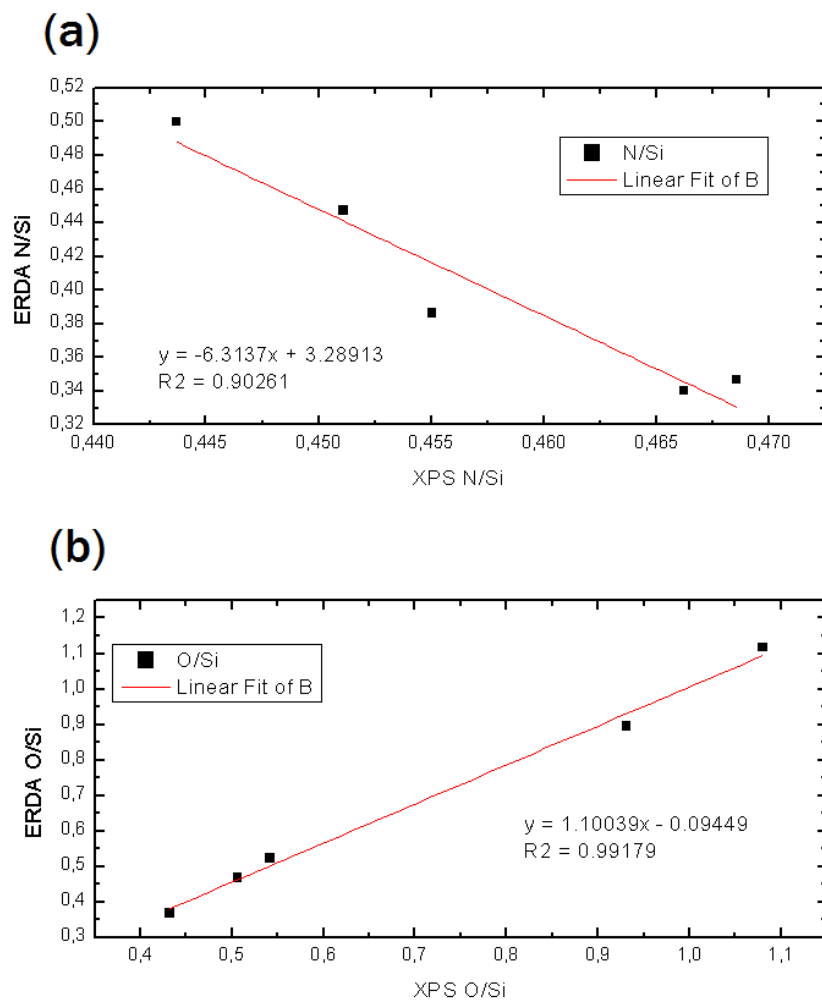


Figure 3.12: Atomic percentage ratios extracted from XPS compared to ERDA data for N series. (a) N/Si ratio, (b) O/Si ratio.

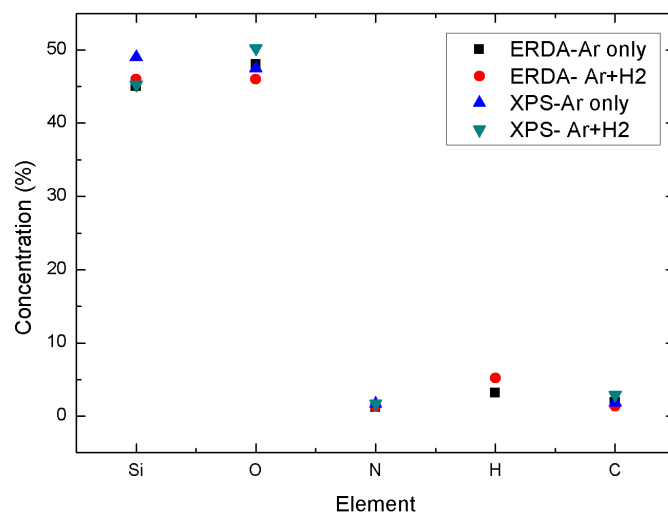


Figure 3.13: Atomic percentages extracted from XPS compared to those extracted from ERDA data for samples prepared by sputtering.

3.2.3 Composition Analysis by FTIR

Fourier transform infrared spectroscopy (FTIR) is a technique to measure the absorption and reflection of a material. The molecules inside the films can be regarded as oscillators, these oscillators are driven by the electric field of the light. Light with frequency that matches the oscillator frequency is absorbed. Absorption spectra yields these oscillator frequencies. From this information it is possible to get a significant information about the bonding structure. This technique uses a broadband light source, but the light passes through an interferometer before the sample. The interferometer transmits some wavelengths and blocks others. By moving the mirror of the interferometer, an interferogram is obtained. Actual absorbance spectrum is the Fourier transform of this interferogram. These spectra are actually a sum of many absorbance peaks that corresponds a different bonds or different vibrational mode of the same bond, and these peaks should be identified. We used PeakFit software to analyze the spectra. The software tries to fit the sum of a number of Lorentzian peaks by changing the width and intensity of the peaks and minimizing the root-mean-square error. We checked the frequency shifts and intensities of selected peaks as well as absorption intensities and areas. We grew films on double side polished, infrared transparent silicon substrates. The films we grew contained Si, O, N, H and C. Some of the peak wavenumbers related to bonds between these element are given in table 3.4. A typical FTIR spectrum of sample H7 is shown in figure 3.14 in the range of 400-4000 cm^{-1} details of which are as follows: Around 450 cm^{-1} Si-O-Si rocking mode and around 650 cm^{-1} Si-H₂ wagging mode, as well as around 850 cm^{-1} Si-O-Si bending and Si-N₃ modes are observed. Si-O stretching mode is observed around 1050, and Si-H stretching mode is observed around 2000 cm^{-1} [17, 18]. Prominent features are Si-O and S-N vibrational modes. Concentration of relevant modes and the oscillator strengths of the said modes define the magnitude of the peaks in the spectrum. It should be noted that the bonding configurations of modes may vary and this will affect the resonance frequency of the absorption peak as well as both tensile and compressive stress.

Absorbance spectra for the films are given in figures 3.15 for the region between 700 cm^{-1} - 1300 cm^{-1} . The peak close to 1050 cm^{-1} is due to Si-O-Si stretching mode, the peak at approximately 805 cm^{-1} is due to Si-O-Si bending mode [19, 20], while the peak around 845 cm^{-1} is due to SiN₃ bond [21, 22]. The peak at 1050 cm^{-1} is visible in C and N series as well. The 850 cm^{-1} peak may be the product of both Si-O-Si and Si-N bonds, but, since it is highest for N series, which has the highest nitrogen content, and the lowest for C series which has the lowest N content we can infer that main contribution to this peak comes from Si-N₃ bonds. For N series, intensity of the 850 cm^{-1} peak exhibit an increasing trend with increasing silicon content, indicating the availability of N due to high concentration of balance N in SiH₄ gas, as opposed to the decreasing trend observed in H series where N supply is limited by N₂O flow rate. However, intensity of the Si-O-Si bond peak at 1050 cm^{-1} increases as the silicon content decrease for all samples. For H series central frequency of this peak decreases as the silicon content decrease. Figure 3.16 shows the correlation between [O]/[Si] from ERDA data and stretching peak position at around 1030 cm^{-1} . There is a linear relationship between [O]/[Si] and peak position. From the fitted line the formula is $[O/Si] = (\omega_{Si-O-Si} + 31.4)/1057$. Since the x-axis of this data is calibrated with ERDA data and gives us the correct O/Si ratio. It is possible to determine O/Si ratio using this formula, if the vibrational frequency of Si-O-Si peak is measured using IR spectroscopy.

Bonding type	Center frequency (cm^{-1})
Si-O-Si rocking	458
Si-H SiH ₂ wagging	650
Si-O-Si bending	812
Si-N ₃ bond	845
Si-O in-phase stretching	1050
Si-O out-of-phase	1150
Si-H stretching	2000-2200

Table 3.4: A list of bond frequencies related to our films.

FTIR is sensitive to hydrogen, and may complement XPS data to determine at least its presence and variation of hydrogen from sample to sample. Hydrogen

contributes to the spectra with Si-H, N-H with Si back-bonding (Si-NH) and O-H with Si back bonding (Si-OH) bonds. Frequency of Si-H wagging mode is at approximately 650 cm^{-1} , Si-OH and Si-NH frequency is about 3500 cm^{-1} , Si-h stretching frequency is about 2200 cm^{-1} (Figure 3.17). A detailed investigation is needed to correlate hydrogen content and FTIR spectra, but as a preliminary analysis we can say that the decrease in the intensity of the Si-H wagging mode peak (Figure 3.18) is correlated to the increase in the intensity of the Si-OH peak (Figure 3.17(c)). Considering the ERDA data, we can assume that the hydrogen content of the films are almost constant for H series. Therefore as we go from H1 to H8, hydrogen is more and more bonded to oxygen with silicon back-bonding or nitrogen with silicon backbonding. Si-H bonds gradually turn into Si-O back-bonded hydrogen and Si-N back-bonded hydrogen bonds. In figure 3.17(b), and We can observe that a more complex structure rises in the Si-H stretching mode region: the spectrum shows several peaks, especially a second peak at higher frequencies becomes more and more prominent with the increasing oxygen content of the film. The reason of this tendency of shifting to the higher frequencies (Figure 3.19) may be the decreasing density of Si-Si bonds. In the film bonds are not isolated, each silicon atom may be bonded to more than one type of atom like another silicon, oxygen or nitrogen atom. It exists then different structural unit denoted as $\text{Si}(\text{Si}_{4-n}\text{O}_n)$ with $0 < n < 4$. Silicon is a relatively heavy atom therefore lowers the frequency of oscillation of Si-H bond. In Si-O-Si bond Si atoms may be bonded to other silicon atoms and decreasing the silicon ratio shift the oscillator frequency to higher values. The same trend as in figure 3.19 is observed for Si-O-Si bending mode, figure 3.20. Increasing N₂O flow rate oxidizes more Si atoms. Si-O bonds that may have other Si atoms backbonded to Si-O-Si will have their backbonded Si atoms replaced by O increasing the vibrational frequency of the Si-O-Si bonds.

FTIR measurements could be an affordable alternative for compositional analysis of PECVD grown hydrogenated oxynitride films, if calibrated by a more direct method like ERDA. It may be possible to detect hydrogen by FTIR to complement XPS compositional analysis. To have an accurate calibration, the effect of all the elements (Si, O, N, H, C) should be discriminated. IR spectroscopy

provides important information on the molecular structure of the films used for formation of Si nanoclusters. Many compositional and configurational parameters may play a role in the formation of Si nanoclusters. Establishing a clear correlation between all these parameters and the formation of nanoparticles is beyond the scope of this thesis. Despite the lack of quantitative results, IR spectroscopy provides important information as the trends concerning the variations of different elements. It is possible to determine whether or not a given bond and hence atomic species remains constant or varies with a process parameter. We find that Si-H₂ wagging mode and Si-H stretching mode frequency are correlated to the N₂O flow rate. We also observed a linear relationship between O/Si ratio and Si-O-Si stretching peak central frequency.

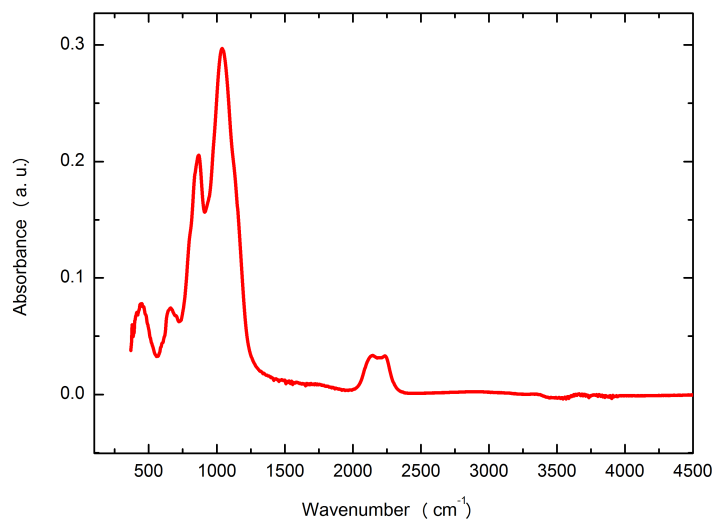


Figure 3.14: Example FTIR spectrum. Sample is H7.

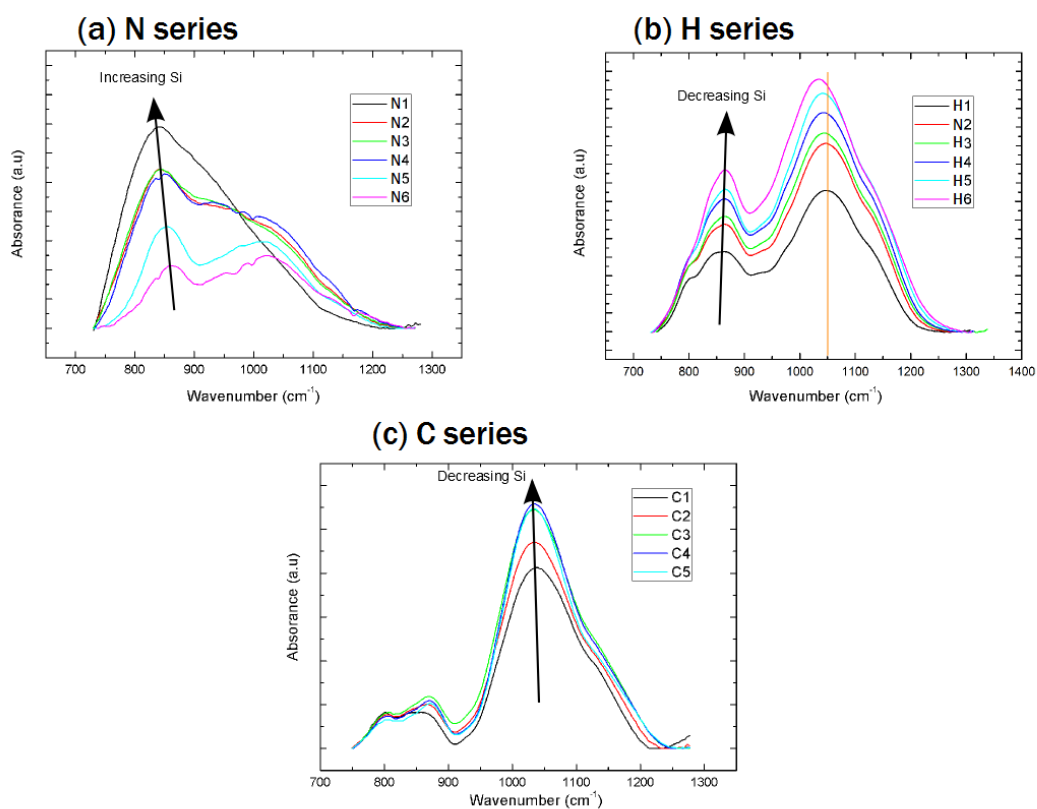


Figure 3.15: FTIR spectra of H, C and N series showing the peaks between 700-1300 nm.

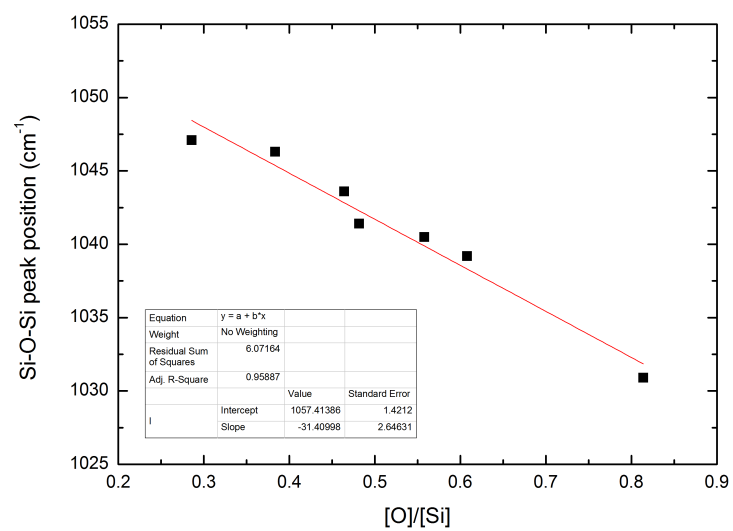


Figure 3.16: Si-O-Si stretching mode peak position for H series.

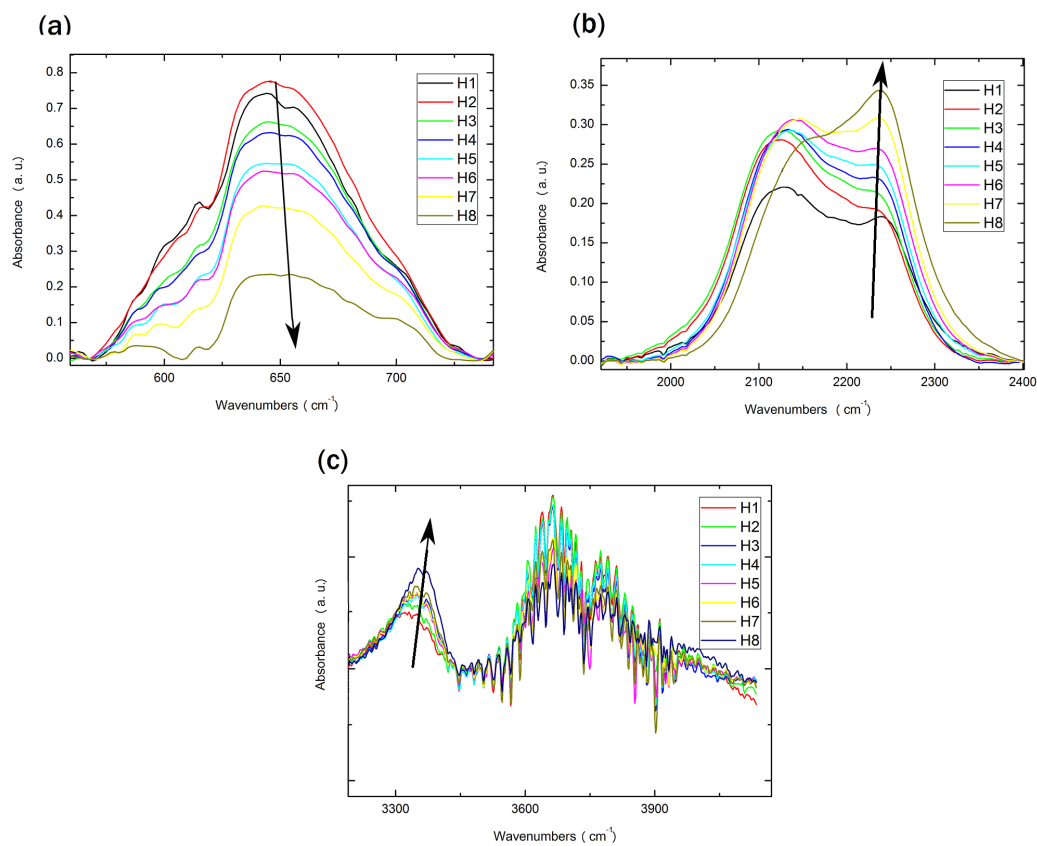


Figure 3.17: FTIR spectra of Si-H wagging mode at 650 cm^{-1} (a), Si-H stretching mode at 2100 cm^{-1} (b) and Si-OH or Si-N stretching mode at 3300 cm^{-1} (c) for H series. The arrows show the direction of increasing or decreasing H content.

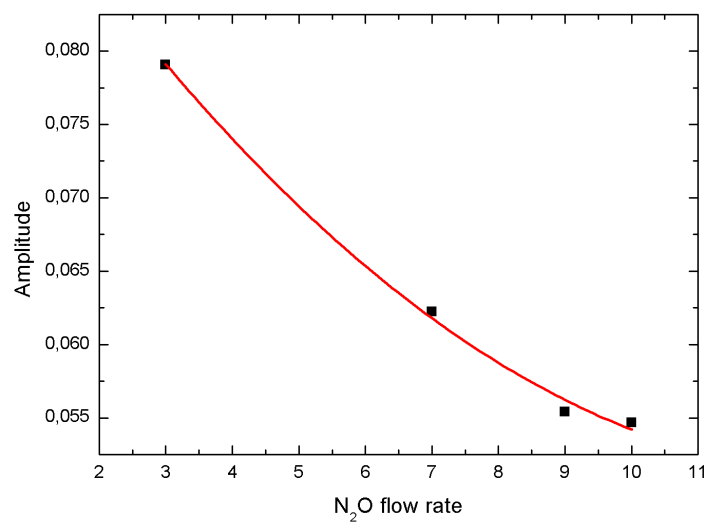


Figure 3.18: Si-H wagging mode absorbance intensity with respect to oxygen to silicon ratio for H series.

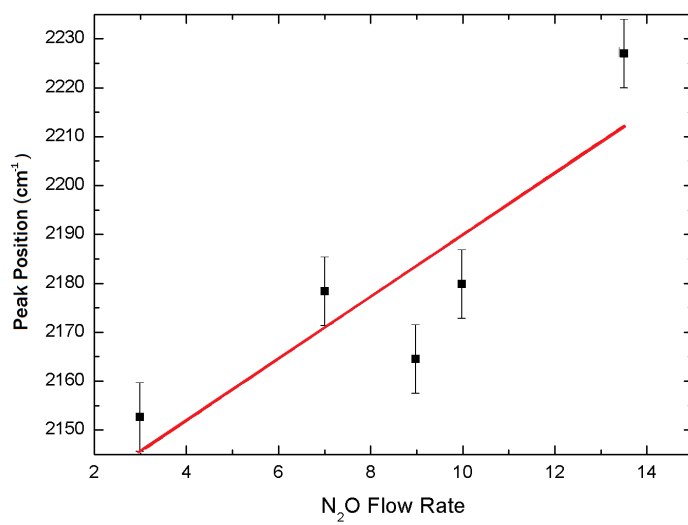


Figure 3.19: SiH₂ stretching mode absorbance central frequency with respect to flow rate of N₂O for H series.

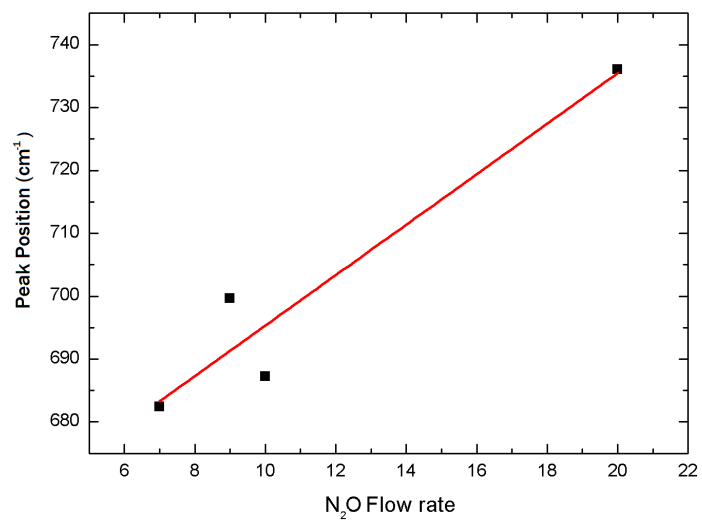


Figure 3.20: Si-O-Si bending mode absorbance central frequency with respect to flow rate of N_2O for H series.

ϵ_1	2.5-3.6
A	10-20
B	0.10-0.14
E_c	3.3-4.0

Table 3.5: Typical range of lorentz fit parameters for ellipsometry.

3.2.4 Determination of Optical Properties by Ellipsometry

Ellipsometry is a technique to measure optical properties including but not limited to index of refraction, extinction coefficient and film thickness of thin films. An elliptically polarized light is incident on the sample and reflected beam is analyzed to obtain the ratio of the s and p polarized components. From this ratio two parameters called Ψ and Δ are obtained. The relationship between Ψ , Δ and the reflected intensities is:

$$\frac{I_p}{I_s} = \tan\Psi e^{i\Delta}$$

I_p and I_s are the ratio of intensity of the incoming and reflected light for p and s polarised light respectively. The software fits the theoretical Ψ and Δ values to the experimental ones by minimizing the root-mean-square error. To calculate the theoretical Ψ and Δ , a model needs to be defined. This model is composed of suspected layers of material making up the sample and uses either pre-measured tables of index of refraction and extinction coefficient of a material or uses a physical model like Lorentz oscillator [23] for these quantities. Lorentz oscillator model assumes that the material is a damped oscillator system, the complex dielectric constant of which is given by;

$$\epsilon^* = \epsilon_1 \frac{AE_c}{E_c^2 - E^2 - iBE}$$

where A is the amplitude, B is the broadening of the oscillator mode, E_c is the vibrational energy, ϵ_1 is the offset energy, and E is the energy of the photon. Expected range of these parameters for SiO_x films are given in table 3.5.

For ellipsometric measurements a J. A. Woollam variable angle spectroscopic

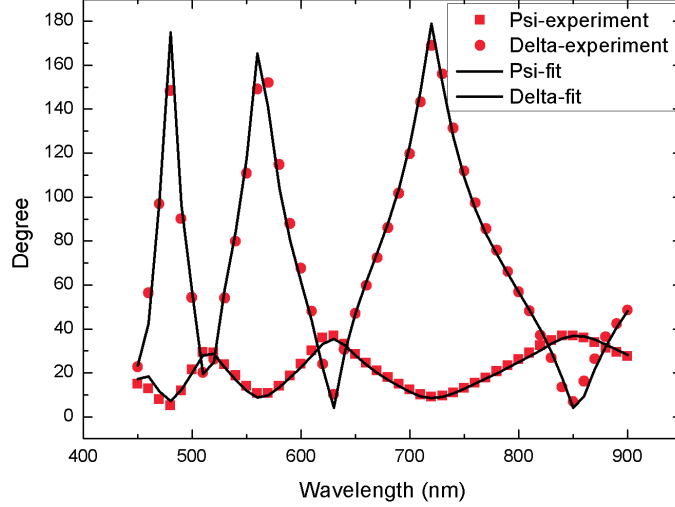


Figure 3.21: Typical raw ellipsometric data with Lorentz oscillator model fit for silicon rich oxide thin films.

ellipsometer (VASE) with wavelength range 300-1700 nm was used. Angle of incidence was set generally between 65-75 degrees. We used silicon substrates, since for some samples grown on quartz, reflection from the uncoated side of the substrate interfered with the signal. From the ellipsometric measurements thickness, index of refraction and extinction coefficient was extracted. Typical experimental and fitted Ψ and Δ data are shown in figure 3.21. Refractive index calculated by fitting Lorentz model to experimental data are given in figure 3.22. In general all refractive indices increase as wavelength gets smaller in accordance with Cauchy law. Extinction coefficients are given in figure 3.23. The extinction coefficients also increase at shorter wavelengths suggesting a resonance in the UV. We further note that increasing the Si content in the films increase the refractive index as well as the extinction coefficient as expected.

These films can also be regarded as a mixture of SiO_2 and Si by effective medium approximation. The refractive index and extinction coefficient can be calculated from linear form of effective medium approximation by the formula;

$$n_{\text{effective}} = xn_{\text{Si}} + (1 - x)n_{\text{SiO}_2}$$

and

$$k_{effective} = xk_{Si} + (1 - x)k_{SiO_2}$$

where x is the ratio of the silicon content, n_{Si} , k_{Si} , n_{SiO_2} and k_{SiO_2} are the refractive index and extinction coefficient of silicon and silicon dioxide. Effective medium approximation therefore shows that the films richer in silicon has refractive index and extinction coefficient closer to the bulk silicon's. This explains the increasing trend observed in refractive index and extinction coefficient. Due to the nitrogen content and high absorption, effective medium approximation cannot give the composition accurately, however comparing the ERDA data to refractive index it is observed that SiO_x films with $x=1$ have a refractive index around 2. Figure 3.22(d) compares the refractive index of hydrogenated and non-hydrogenated films. Hydrogenated films have lower refractive index as lighter hydrogen atoms increase the frequency of oscillator. Extinction coefficients also increase with silicon content in these samples.

We also measured the transmission coefficient at normal incidence by ellipsometry of H series 300nm thick films on quartz substrates (Figure 3.24). We observed that transmitted light at 490 nm is inversely proportional to the refractive index of the film since the light is reflected more at the interfaces that has a larger index difference at both sides. The transmission is less for the films that has higher silicon to oxygen ratio. The transmission coefficient was found to be between 30% and 85%.

We correlated Si, O, N and H content of the films from ERDA measurements and the refractive indices at 900 nm (since the index is relatively constant around 900 nm) from ellipsometric measurements using Eureka software. By fitting linear coefficients to our dataset, we found an empirical relationship for the refractive index:

$$n = 0.05028 * H + 0.02732 * Si + 0.00491 * O - 0.01125 * N$$

where H, Si, O and N are the atomic percentages of these elements. Figure 3.25 shows the index values calculated from the formula and measured by ellipsometry. Mean square error is found as 0.00117 (data of sputtered sample are

excluded). The formula suggests that effect of the hydrogen is high, and proportional to the index. However, we expect hydrogen to decrease the refractive index, in accordance to figure 3.22(d). The hydrogen content of these films generally increase as the silicon content increases, according to the ERDA results. Hence, this relationship may be the applicable to PECVD method only, and may not be applicable for thin films produced by different methods. Indeed, sputtered samples (circled in blue) do not exhibit the same correlation.

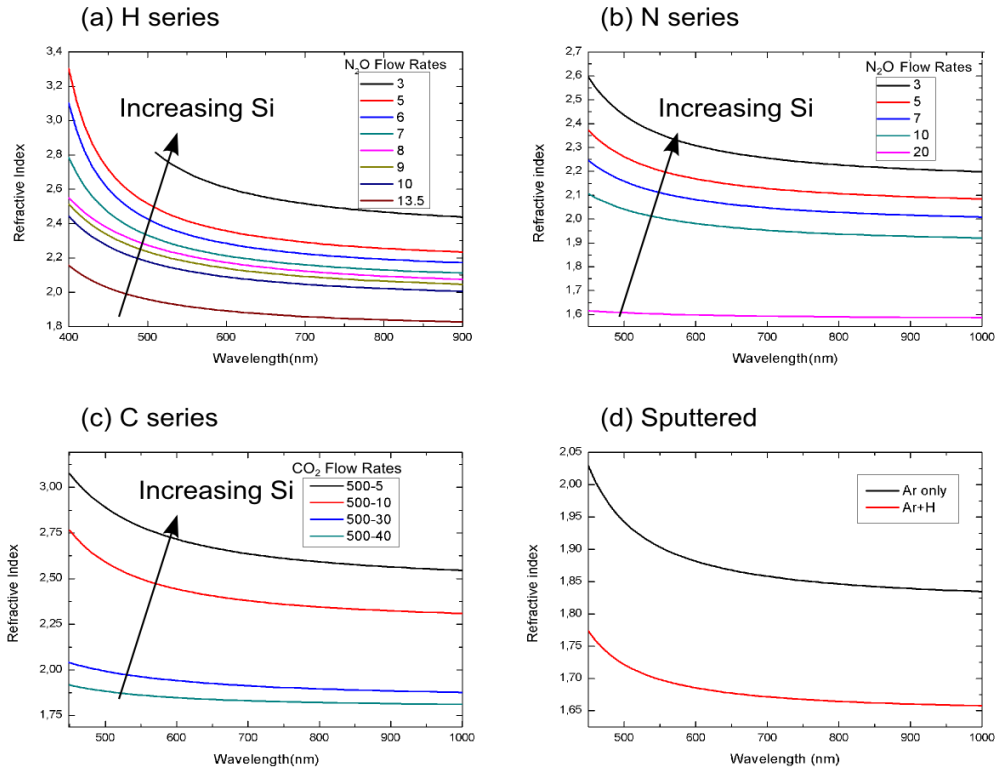


Figure 3.22: Refractive index as a function of wavelength for different N_2O and CO_2 flow rates for H, N, C series and sputtered samples. Flow rates are given in sccm in the inset. Growth parameters are given in section 3.1.

Growth rates calculated from thicknesses are given in figure 3.26. Growth rate of N series is relatively constant and around 80nm/min. Growth rates are higher for N series ($SiH_4:N_2+N_2O$) than H series ($SiH_4:H_2+N_2O$), as nitrogen also contributes to the film growth by forming silicon nitride. C series ($SiH_4:H_2+CO_2$) growth speed is lower than H series, probably due to C-O bond enthalpy being higher than Si-O. Decomposition of CO_2 also require more energy than of N_2O . For C and H series, growth rate increase as the film composition gets closer to

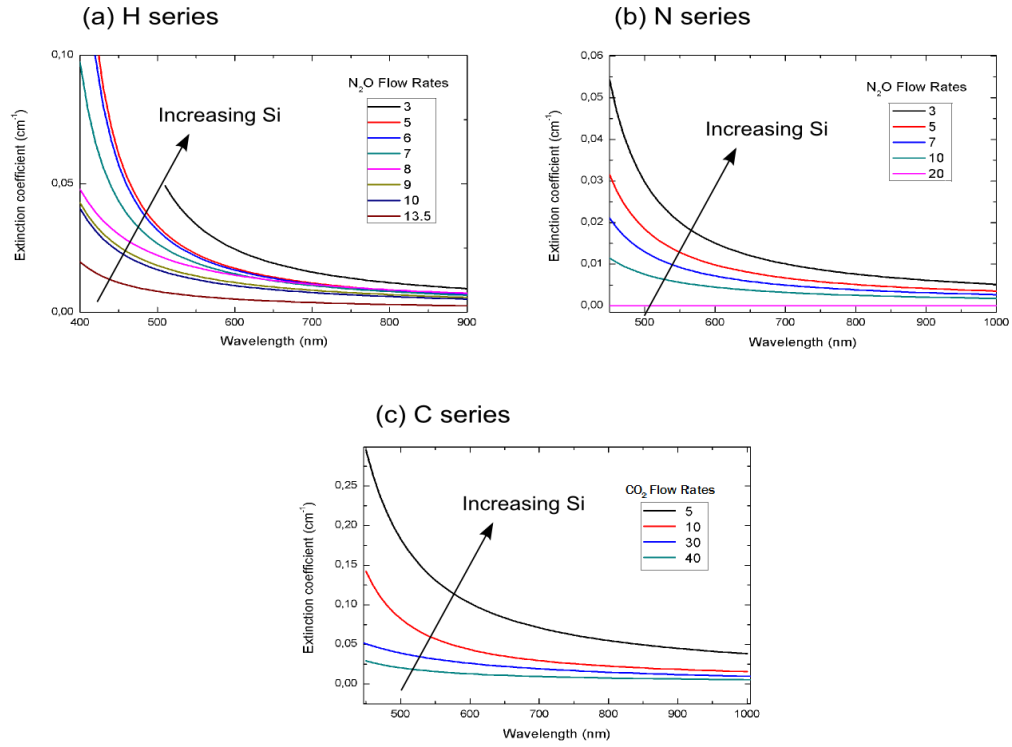


Figure 3.23: Extinction coefficient as a function of wavelength for different N_2O and CO_2 flow rates for H, N, and C series. Flow rates are given in sccm in the inset. Growth parameters are given in section 3.1.

the stoichiometric ratio due to the larger number of oxygen ions inside the growth chamber, however for N series growth chamber may be saturated by nitrogen ions so that the rate does not change as much. About ten percent fluctuation may be the result of high growth rate.

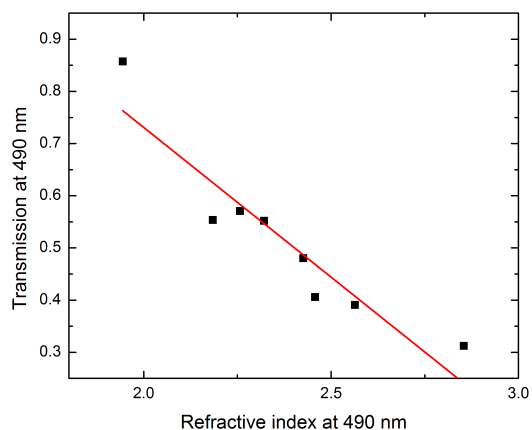


Figure 3.24: Transmission coefficient as a function of refractive index at normal incidence by ellipsometry of H series on quartz substrates.

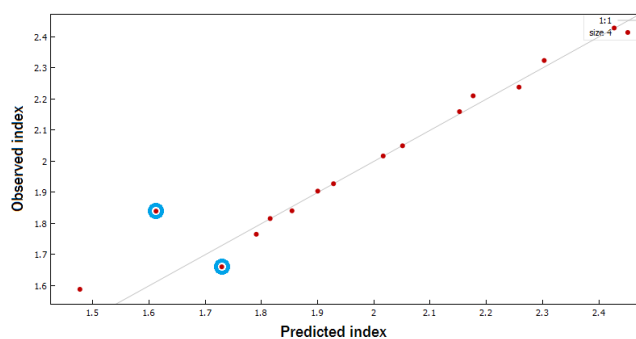


Figure 3.25: Observed vs predicted plot of refractive index at 900 nm. X axis is the values calculated from the formula $n = 0.05028H + 0.02732Si + 0.00491O - 0.01125N$. The points circled in blue are data of the sputtered samples.

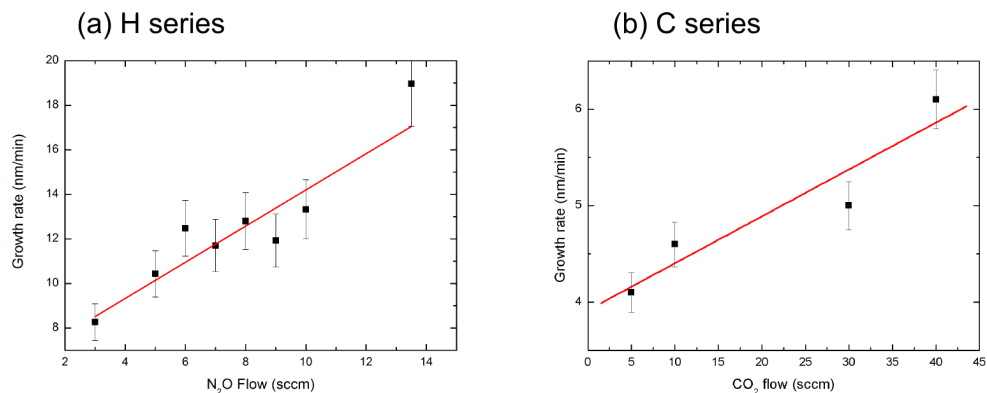


Figure 3.26: Growth rate of H and C series with respect to N_2O and CO_2 flow rates with all other parameters held constant.

3.3 Conclusion

We have explained the PECVD and sputtering methods for silicon rich oxide thin film growth. We have listed the growth parameters of 4 series of samples (Table 3.1 and 3.2): H series (grown by precursor gases $\text{SiH}_4:\text{H}_2+\text{N}_2\text{O}$), N series (grown by precursor gases $\text{SiH}_4:\text{N}_2+\text{N}_2\text{O}$), C series (grown by precursor gases $\text{SiH}_4:\text{H}_2+\text{CO}_2$) and sputtered samples. H, C, and N series are made by varying the flow rates of N_2O or CO_2 , whereas sputtered samples were grown either by pure argon or by hydrogenated argon. Therefore composition of each sample within the series had to be identified. The films were analyzed by possibly the most accurate method for compositional analysis, ERDA, and the results are listed in table 3.3. We have shown that lower N_2O or CO_2 flow rates results in higher silicon content. N series contains a large amount of nitrogen (about 17%), H series contains a moderate amount (3-12%) of nitrogen, and C series contains a small amount (1-2 %) of it. PECVD grown films contains hydrogen between 8% to 20 %. Sputtered samples have Si/O ratio close to 1, and hydrogenated sample contains slightly higher amount of hydrogen. Due to limited access of ERDA, we tried alternative methods like XPS and FTIR. XPS is not sensitive to hydrogen, but oxygen and nitrogen ratios can be very precisely measured, indeed, O/Si ratios are close to the ERDA results (Figure 3.10 3.11 and 3.12). N/O ratios can also be found by calibration of XPS data according to ERDA. We conclude that if hydrogen content is known thorough an analytical technique such as ERDA, as in our case, XPS data may yield the full composition. FTIR is sensitive to hydrogen, hence we propose that FTIR can complement XPS method. We have shown that IR absorbance intensity and vibrational frequencies of Si-H wagging mode at 650 cm^{-1} , Si-H stretching mode at 2100 cm^{-1} and Si-NH and Si-OH vibrational mode at 3300 cm^{-1} varies with O content. We also observed that Si-O-Si stretching mode peak position at 1050 cm^{-1} is correlated with the O/Si ratio of the film. Finally we have analyzed the thicknesses, refractive indices and extinction coefficients of all samples by ellipsometry. We found that both refractive indices and extinction coefficients increase with silicon content for all series. We have found the growth rates of the films from the measured thicknesses and growth times, and observed that growth rates increase with $\text{N}_2\text{O}/\text{SiH}_4$ and

CO_2/SiH_4 flow rate ratios. It seems that it is also possible to estimate the Si of the film from refractive index value (Figure 3.25).

Nanoparticle formation critically depends on composition of the film. In this chapter we have examined the composition and other properties of as grown films. In the next chapter, we will explain the furnace annealing and laser processing methods for nanoparticle formation, and focus on the effect of composition on the Si nanoparticle formation.

Chapter 4

Nanostructure Formation

For nanoparticle formation, we have processed the Si rich oxide thin films by two different methods: continuous wave laser processing and thermal annealing. Laser irradiation was done by varying power densities, while thermal annealing was done by varying the annealing temperature and time. Formation of Si nanoparticles was characterized by Raman spectroscopy. Nanocrystal formation threshold was determined as a function of laser power density and dwell time in the case of laser annealing and temperature and annealing time, in the case of thermal annealing. The effect of the composition and hydrogen content on nanocrystal formation threshold was analyzed. The main purpose of the thermal annealing was to compare the nanocrystalline Si formation threshold to laser processing method threshold. Threshold values obtained from laser processing were compared to thermal annealing. Spatial distribution of nanoparticles on scanned lines were analyzed by Raman spectroscopy, Dektak and optical microscopy.

4.1 Thermal Annealing

Samples were annealed in an Annealsys SprayCVD-050 rapid thermal processor up to 1200°C under 200 sccm argon flow. Annealing steps are as follows:

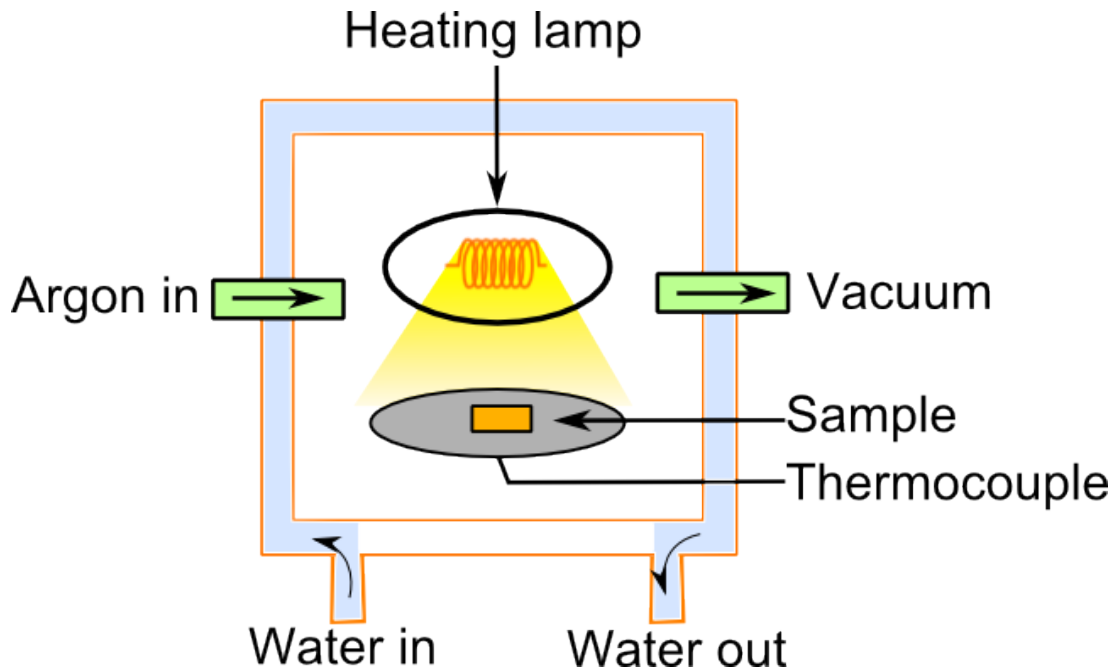


Figure 4.1: Schematic diagram of rapid thermal processing system.

Step 1 Purge: 120 sec. 200 sccm Ar flow

Step 2 Moist Removal Temp. Rise Up: 70°C in 1 sec.

Step 3 Moist Removal: 70°C for 60 sec.

Step 4 Temp. Rise Up: 520°C in 5 sec.

Step 5 Temp. Rise Up: 900-1200°C in 12 sec.

Step 6 Annealing All steps are done under 200 sccm pure argon flow.

This rapid thermal processing system uses a flashlamp to heat the sample (Figure 4.1). A thermocouple measures the temperature near the sample and a PID temperature controller applies current to the heater accordingly. Argon gas flows into the chamber at a specified flow rate. The chamber is constantly vacuumed to keep the pressure fixed. Chamber walls are cooled by controlled water flow to prevent overheating. At first, the argon flow removes the oxygen inside the chamber then a low power is applied to remove moisture. Afterwards, the temperature is increased at a constant rate; to 520 °C in 5 sec then to 1200 °C in 12

sec. During the annealing step the temperature is constant. When annealing is done, the heater is turned off and the sample cools under argon flow.

H series, C series and sputtered samples (on quartz substrates) were annealed under temperatures between 1000 to 1200 °C for different annealing times. The samples used in this experiment are H7, C3 and sputtered samples (see table 3.1). These samples were chosen to have a x value of $\text{SiO}_x\text{N}_y\text{H}_z$ closest to 1. After the deposition of the thin films on the substrates, each sample was annealed at different times and temperatures. Formation of the nanocrystalline silicon depends on both temperature and time and is expected to exhibit an Arrhenius-like behavior (i. e. the transition rate obeys Arrhenius rate equation $k = Ae^{-E_a/k_B T}$ where E_a is the activation energy, which is the energy needed to form silicon nanocrystals, k_B is the Boltzmann constant and A is a pre-exponential factor that depends on the reaction. Linear relationship between $\ln(k)$ and T^{-1}) is therefore expected.

4.1.1 Raman Characterization

To confirm the formation of nanocrystalline silicon, we used Raman spectroscopy. Raman spectroscopy is a method used to analyze of the vibrational modes of molecular and crystalline samples by light scattering. Raman scattering is basically the inelastic scattering of light from phonons in crystals. Two types of Raman scattering exist: if during the scattering a phonon is created, this is called Stokes scattering, if it destroys a phonon, it is called anti-Stokes scattering. The scattering process conserves both momentum and energy however, photons lose energy and momentum after Stokes scattering. Momentum lost is equal to the momentum ($\hbar k$) of the phonon created. Therefore the wavenumber of the created phonon can be calculated from the formula:

$$k_p = k_i - k_s$$

where k_i is the wavenumber of the incoming photon, k_p is the wavenumber of the phonon and k_s is the wavenumber of the scattered photon.

A schematic of the experimental setup for Raman spectroscopy is shown in figure 4.2. For Raman spectroscopy a monochromatic light source is provided by a laser. The laser beam is focused on the sample using a microscope. Scattered light is collected by a collection lens. The monochromator has a light entrance slit on which the laser is focused. Light is dispersed by a grating into its wavelengths and a CCD measures the intensity of light at certain wavelength intervals.

From a Raman spectrum it may be possible to obtain information about chemical bonds, crystallization, particle size, stress and even temperature. A typical Raman spectra of processed SiO_x sample is shown in figure 4.3. For these measurements, the films were grown on quartz substrates since silicon substrates make it difficult to distinguish the Raman signal coming from the nanoparticles and the substrate. In this spectra 4 peaks are observed: crystalline silicon peak between $510\text{-}520\text{ cm}^{-1}$ (bulk silicon TO Raman frequency is 521 cm^{-1}), amorphous silicon peak around 490 cm^{-1} , and possibly a peak that indicates an intermediate state between crystalline an amorphous peak at around 500 cm^{-1} . The broad peak at around 450 cm^{-1} belongs to the fused quartz substrate as it can be deduced from the as grown films which have only this broad peak. As-grown films have only the fused quartz peak in this range. After annealing at the lowest temperature an amorphous peak is observed. At higher temperatures, intermediate and crystalline peaks are also observed.

In order to find the threshold for nanocrystal formation, many samples at different temperatures were annealed in a nitrogen purged furnace for different times. In these experiments, we measured crystalline transition time by observing the formation of crystalline silicon peak using Raman scattering (figure 4.3). We defined the threshold as the annealing time that crystalline peak makes a visible shoulder in the Raman spectrum. Above this threshold crystalline peaks intensifies, narrows and shifts towards 521 cm^{-1} . As an example, development of the Raman peak for sample H7 annealed at $1150\text{ }^\circ\text{C}$ for different annealing times is given in figure 4.3. We observe that the as grown sample exhibits a broadband scattering spectrum, spanning the wavenumber range of $300\text{-}500\text{ cm}^{-1}$ typical of a quartz substrate, as well as the density of states of the amorphous film (figure 4.3(a)) superimposed onto each other. As the annealing time is increased we

find a new peak emerging beyond 500 cm^{-1} superimposed onto the as grown broadband spectrum (figure 4.3(b-c)). Increasing the annealing time further, this newly emergent peak becomes more prominent and shifts towards 521 cm^{-1} (figure 4.3(d)), typical of nanocrystals. Longer annealing times result in full-fledged Raman line of silicon optical phonon.

Figure 4.5 is constructed using the results of many threshold determination experiment. It represents the annealing times needed to observe a nanocrystalline peak in the Raman spectra as a function of the annealing temperatures for four different types of samples prepared using PECVD and sputtering. Dotted lines are linear fits to the experimental points. The PECVD grown samples that use nitrous oxide and carbon dioxide have different amounts of hydrogen in them. Sputtered samples use pure argon and argon with 25 % hydrogen, to understand the role of hydrogen on the nanocrystal formation. From the comparison of hydrogenated and non-hydrogenated sputtered samples, we can directly conclude that hydrogen lowers the crystallization threshold. We observed that H7 has the lowest threshold while C3 follows it, and hydrogenated sputtered sample has a lower threshold than non-hydrogenated sputtered sample. These rates explain the role of hydrogen. As hydrogen is a light atom, it can move inside the oxide easily, breaking bonds and catalyzing the phase separation, therefore decreasing the activation energy for the formation of Si nanocrystals[24, 25]. The order of hydrogen content in our samples that lead to lower thresholds for nanocrystal formation is $H > C > \text{hydrogenated sputtered} > \text{non-hydrogenated sputtered}$, with the highest threshold being the last. The inverse of this order is valid for threshold times, indicating the facilitative role of hydrogen in phase separation.

In the next section we will explain the laser processing method and lastly compare it to the thermal annealing.

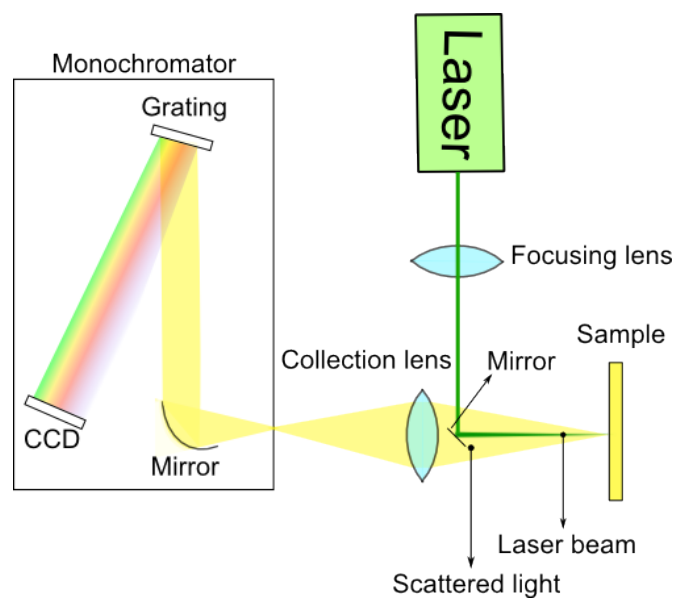


Figure 4.2: Schematic of Raman spectroscopy setup.

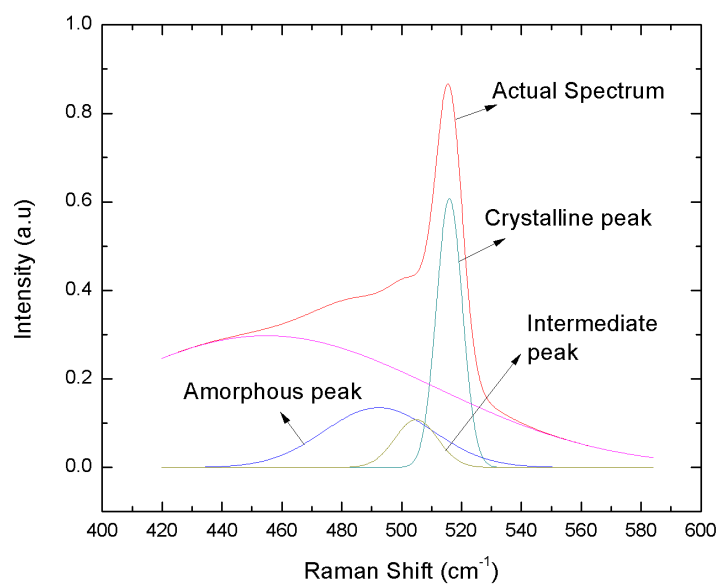


Figure 4.3: A typical Raman spectra of processed SiO_x samples.

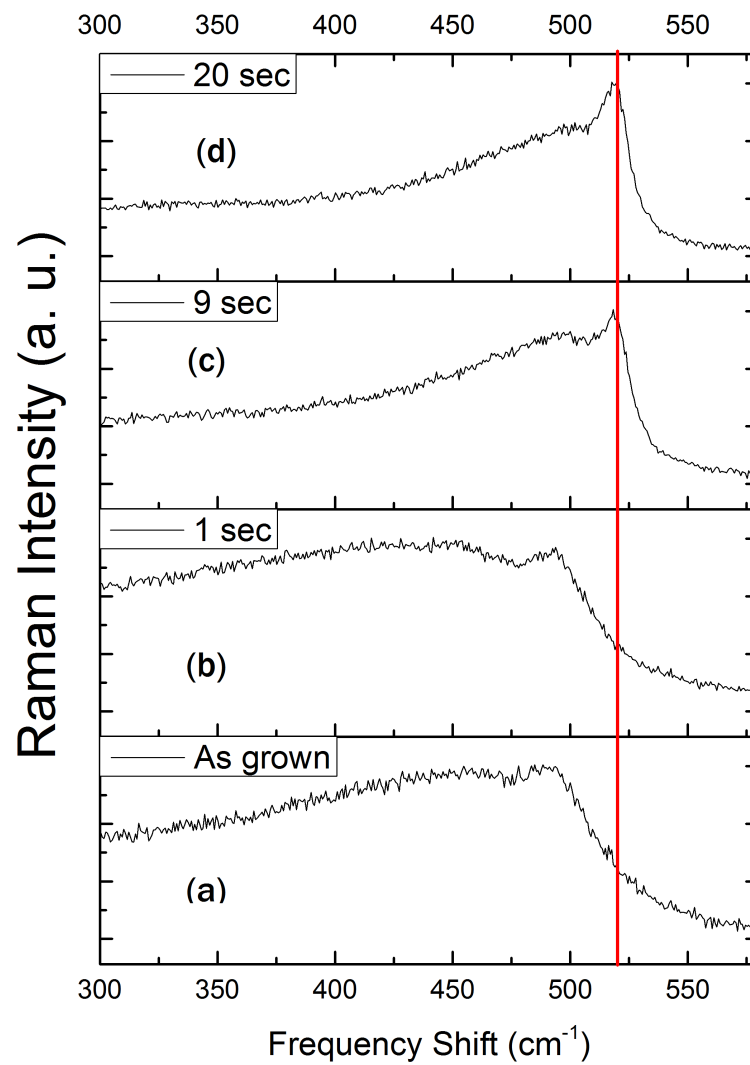


Figure 4.4: Raman spectra of sample H7 annealed at 1150 °C for different annealing times.

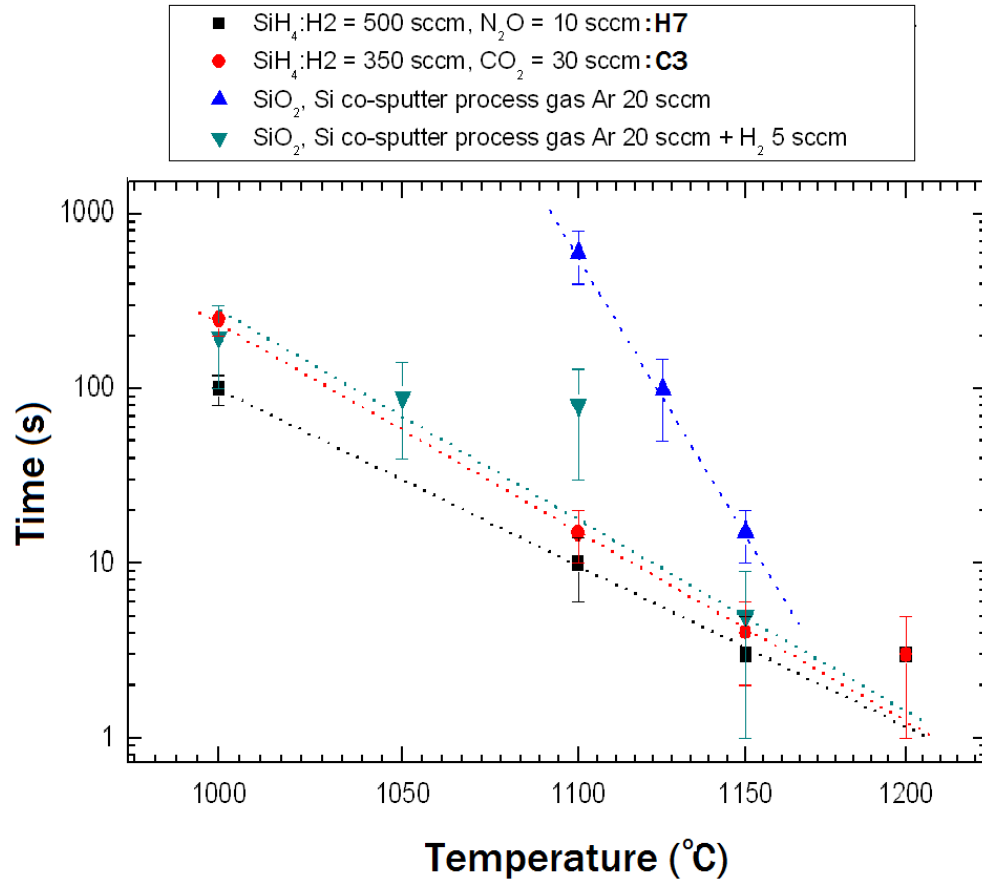


Figure 4.5: Phase transition diagram for the formation of silicon nanoclusters obtained from Raman spectra of furnace annealed samples.

4.2 Laser Processing

Lasers can be used to heat an absorbing material and hence, can be used to crystallize amorphous silicon [26, 27, 28, 29]. Laser processing has some advantages over furnace annealing. It heats the film locally avoiding the heating of the whole substrate. It is possible to form micrometer size patterns, and Raman characterization can be done on the same setup. In this study, we scanned different samples by varying the laser power density. Scanned lines were characterized by Raman spectroscopy, Dektak profilometer and optical microscopy. In the following section, we will discuss the effect of composition of the thin films and laser power on Si nanoparticle formation.

Laser processing was done by 488 nm line of an argon ion laser. Laser beam was focused on the samples by an inverted optical microscope. The beam was expanded before entering the microscope to fully cover the entrance pupil of the microscope objective for better focusing. Spot size was measured using a silicon photodetector and by scanning a razor edge over the spot. A dichroic mirror that reflects 488 nm and transmits longer wavelengths was used to direct laser beam on the samples and collect the Raman scattered light. Raman spectra of the scanned lines was taken using the same setup. A monochromator with a CCD with resolution 2 cm^{-1} was used to collect data. The laser power was measured by a calorimetric power-meter. Scanning of the samples under the laser beam was done by a motor controlled XY stage. A Labview program was written to control the speed and scanning pattern. In the same setup, optical images were taken by a in-situ camera. Figure 4.6 is the schematic of the experimental setup.

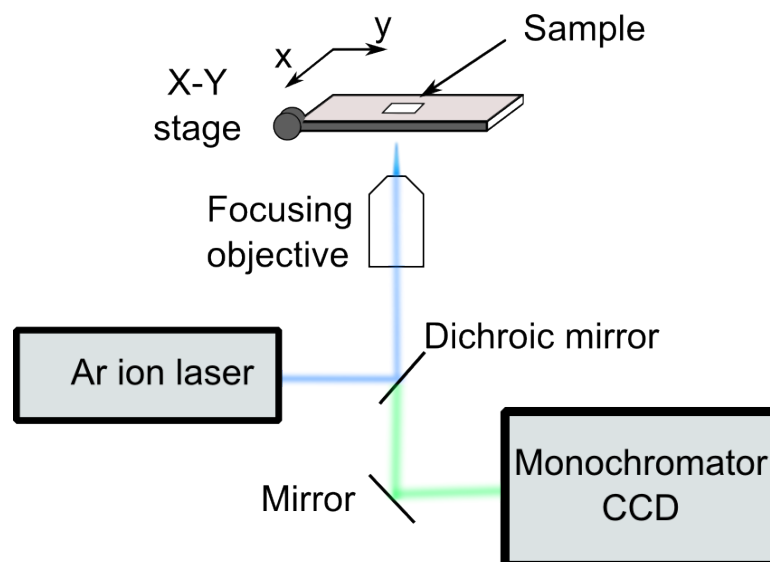


Figure 4.6: Experimental setup of laser processing.

4.2.1 Scanned Zone Characterization

Figure 4.7 is a typical optical image of the scanned lines. Each line was scanned by a different laser power density. When nanocrystalline silicon is formed (confirmed by Raman spectroscopy) generally the effect of the laser is visible on the image. As laser power is increased, lines become wider and more visible. In figure 4.7, the power density decreases towards the bottom of the figure except for the lowermost two which were scanned at higher power densities. We should note that the appearance of the scanned lines also depends on the substrate. On BK7 glass or borosilicate glass, laser scan caused formation of cracks and/or bubbles. We used fused quartz substrates that does not cause these defects.

Figure 4.8 shows Dektak and Raman data of a sample scanned with laser power densities of 38, 48, 51 and 102 kW/cm². Connected black dots are normalized intensities of nanocrystalline Raman peaks. Red dots are Dektak profilometer measurements. Optical images in the background were scaled to match the Dektak profiles. Dektak profiles indicate that scanned lines shrank by a few percent after the laser irradiation. At higher power densities, extra material appears to be deposited at the sides of the scanned zone. It is well known that PECVD grown sample contain a lot of voids. This 5 percent shrinking may be a mechanical effect due to the compacting of the atoms to fill the voids. Raman profiles are consistent with Dektak profiles, nanocrystalline Si peak is observed in laser scanned zones and nanoparticle formation zone gets wider as the power increases. At yet higher power densities (Figure 4.9) material deposition to the sides of the scanned region increases, which may now be due to melting, and nanocrystalline Si profile exhibits a three-peak structure: Raman intensity is the highest in the middle and at the edges of the scanned zone, but vanishes away from the scanned zone. This may indicate formation of three crystalline nanowires and its cause may be non-uniform heating of laser beam. Thermal gradients may cause Si atoms to form nanocrystallites at three distinct locations. At this high power the scanned zone probably melts and some of the silicon atoms tend to diffuse and crystallize at the cooler edges. As the beam moves forward, the middle of the scanned zone solidifies the last, causing silicon atoms to remain in this zone and

solidify in the middle. The origin of this formation needs to be studied further.

We have also laser scanned different lines on the samples by varying the power density. After scanning, the stage was moved back to the middle of the scanned line, and Raman spectra was taken at a much smaller laser power density (smaller than $1\text{kW}/\text{cm}^2$) to prevent heating during Raman scattering. Figure 4.10 allows us to deduce the temporal evolution of the Raman scattering from scanned H3 sample. At low power density, amorphous peak is as visible as nanocrystalline peak, at highest power density, nanocrystalline peak becomes more apparent and intermediate state peaks appear. We used PeakFit software to deconvolute the spectra and identify the peaks. The magenta line in deconvoluted spectra is due to fused quartz substrate. Cyan lines are due to the crystalline Si peak, dark blue lines are the amorphous silicon peaks, and the green lines are the peaks due to intermediate states between amorphous and crystalline Si. As the nanoparticle formation is expected to have an Arrhenius type reaction rate, at higher temperatures the formation rate is expected to be higher. Therefore keeping the dwell time constant at 1 second and varying the power density, shows the temporal evolution of nanocrystalline peak formation. At first nucleation occurs but the precipitated nuclei is not completely crystalized and is not Raman visible. Crystallization occurs gradually in time, and as the nanostructures grows intermediate states forms [30].

To analyze the role of composition on nanocrystal formation, we have laser processed samples from H series with different O/Si content. Figure 4.11 and 4.12 shows the effect of the composition on nanocrystalline peak formation. In figure 4.11, Raman spectra taken from lines with varied power densities of samples H1, H3, H5 and H7 are shown. Dwell time (beamwidth/scan speed) is 1 second. Crystalline peak becomes more prominent with increasing power density and shifts to the higher frequencies getting closer to the bulk silicon Raman frequency shift at about 521 cm^{-1} for all samples. This shift can be attributed to increasing crystalline quality and size of the nanocrystals. We note that in all Raman spectra compressive stress[31] during cooling after the formation of nanostructure may also contribute to the shift of the Raman peak. We assume

that the magnitude of the stress is the same in all processed samples, and samples can be Raman compared. Linewidths are larger than bulk silicon (between $10\text{-}17\text{ cm}^{-1}$ compared to 2.8 cm^{-1} of bulk). This suggest that nanocrystallites show a size distribution. The zone that Raman spectra was measured is small, yet contains various sizes of nanocrystalline silicon particles. These particles with different phonon frequencies, add up to a wide Raman signal. Figure 4.12 shows the nanoparticle formation threshold, peak position, signal amplitude and Raman linewidths with respect to the O content obtained from ERDA results for H series. Oxygen facilitates nanocrystal formation until the film composition reaches 25 at.% oxygen. It may decrease the activation energy of the formation and speed up the nanocrystal formation at lower temperatures. Peak position blue-shifts and linewidths become narrower indicating that nanoparticles are closer to the bulk like sizes with higher oxygen content, then this trend is reversed as it was observed in the literature [32]. Raman signal amplitude is also higher indicating that more of the silicon precipitated into crystalline particles.

Figure 4.13 compares the non-hydrogenated and hydrogenated sputtered films for nanoparticle formation threshold. Similar to H series films, Raman peak position shifts to the higher frequencies with increasing laser frequencies. Threshold for nanocrystal formation of hydrogenated film is 42 kW/cm^2 while threshold for nanocrystal formation is about 52 kW/cm^2 for non-hydrogenated sample. Particle formation in the non-hydrogenated sample is also more sudden. Figure 4.14 shows the evolution of Raman spectra with increasing power density for sample C3. This data is consistent with what we obtained from furnace annealing. Nanoparticle formation threshold of laser processing for different samples and their hydrogen content are shown in table 4.1. Except for small the shift in the Raman frequencies between C3 and hydrogenated sputtered sample, the order of threshold is consistent to the results of furnace annealing (Figure 4.5). In the thermal annealing method, we had concluded that hydrogen facilitates nanocrystalline Si formation in annealed silicon rich oxides. Comparing the threshold power densities and hydrogen content in table 4.1, we can come to the same conclusion for samples that were processed with cw laser processing method.

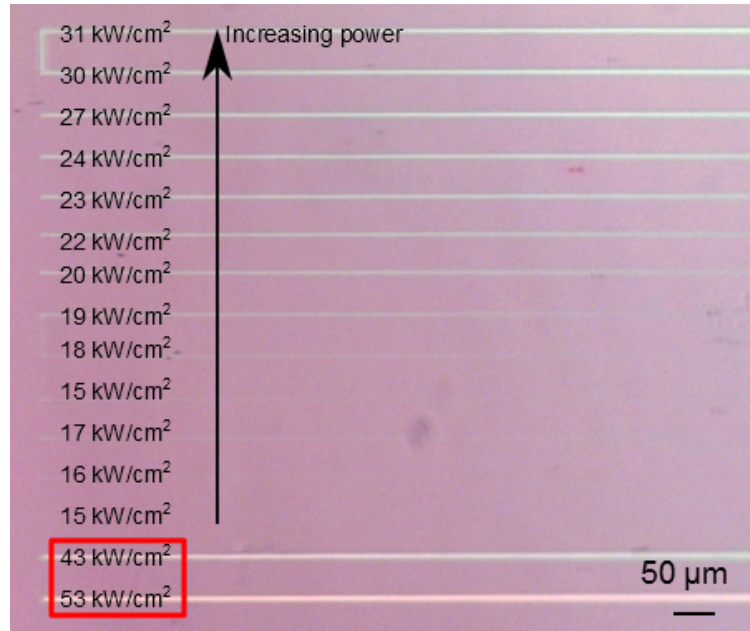


Figure 4.7: An example of optical microscopy image of laser processed lines. Dwell time is 1 second.

Sample	Threshold power density	Hydrogen content (at. %)
H7	$35.5 \pm 2 \text{ kW/cm}^2$	11
C3	$44.5 \pm 2 \text{ kW/cm}^2$	8.4
Sputter Ar + H ₂	$42 \pm 2 \text{ kW/cm}^2$	5.2
Sputter Ar	$52 \pm 2 \text{ kW/cm}^2$	3.2

Table 4.1: Nanocrystalline peak formation threshold for laser scanned samples.

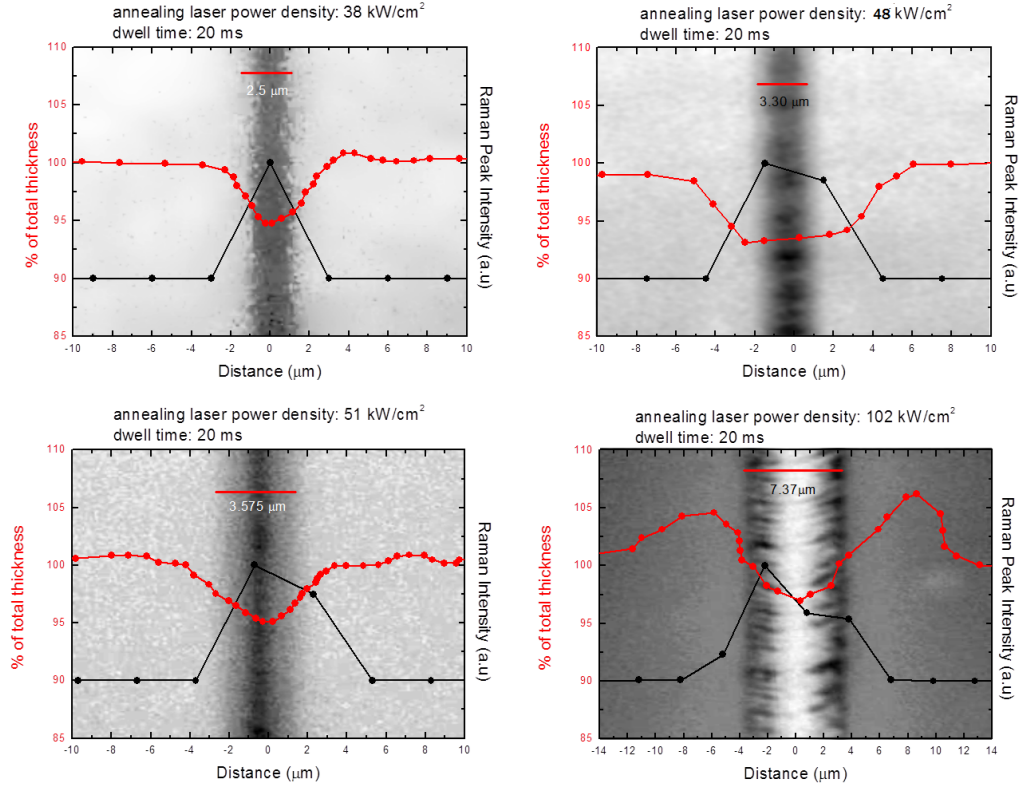


Figure 4.8: Microscope images of the processed lines with Dektak and superimposed Raman intensity profiles.

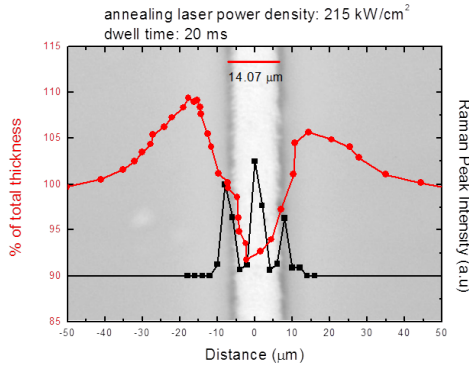


Figure 4.9: Microscope image of high power (215 kW/cm²) processed line with Dektak and superimposed Raman intensity profile.

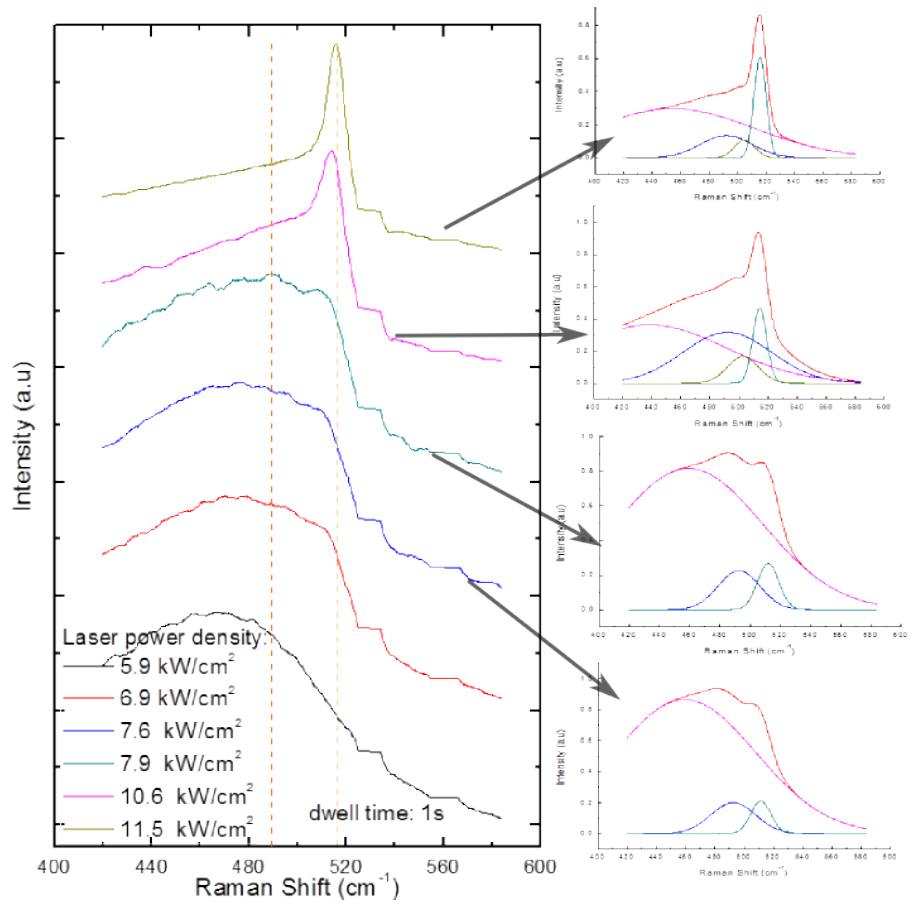


Figure 4.10: Laser power density dependence of Raman spectra of 1 sec laser processed zone in sample H3.

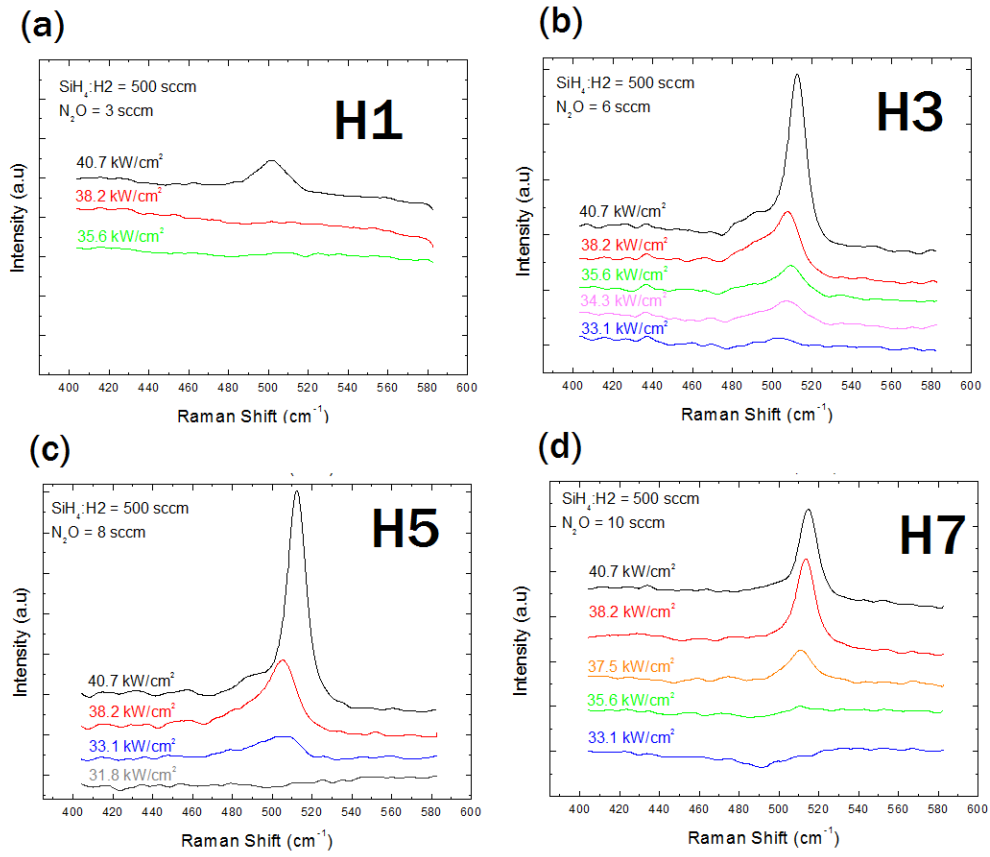


Figure 4.11: Raman spectra after processing by various laser power densities for H series.

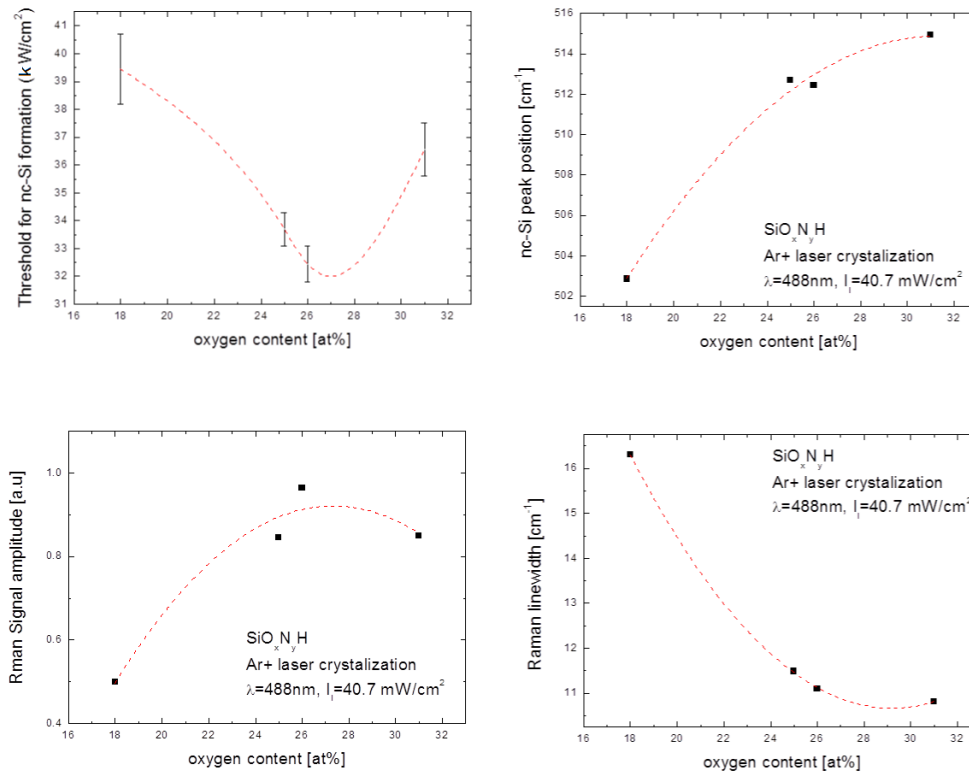


Figure 4.12: Threshold, peak position, signal amplitude and linewidth after laser processing films with varying oxygen content for H series. Dwell time is 1 seconds. Power density for (b), (c) and (d) is 40.7 mW/cm^2 .

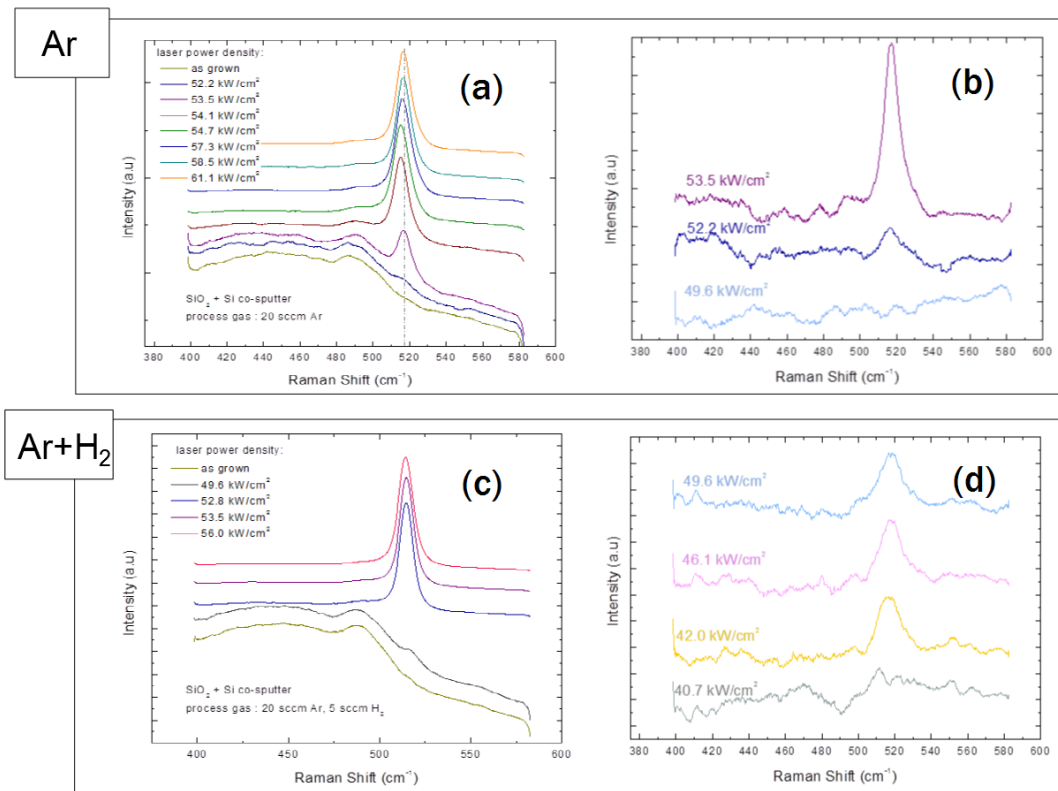


Figure 4.13: Laser power density dependence of Raman spectra of 1 sec laser processed sputtered non-hydrogenated (a,b) and hydrogenated (c,d) samples.

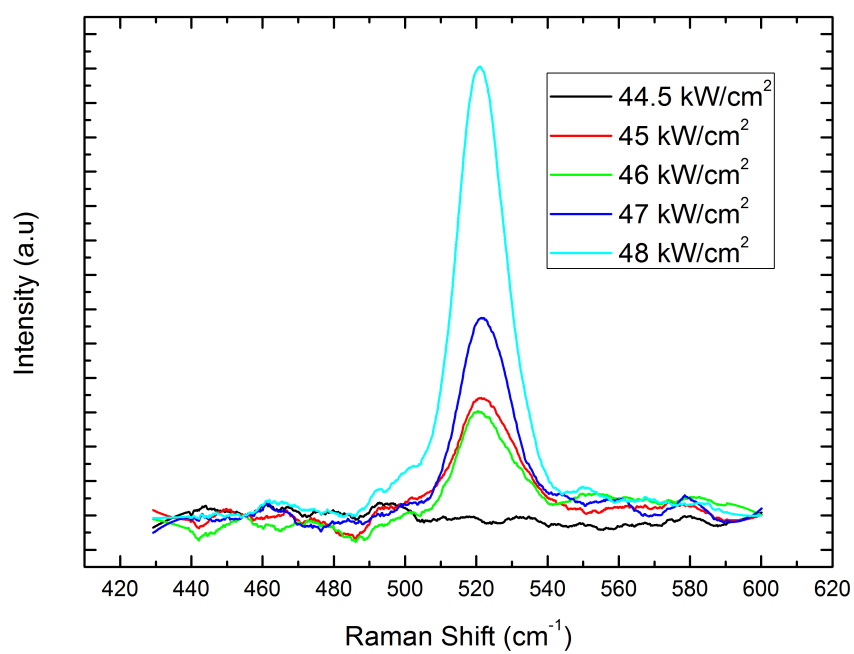


Figure 4.14: Laser power density dependence of Raman spectra for C3 for 1 sec dwell time laser processing.

4.3 Conclusion

In this chapter we explained the thermal annealing and laser processing methods for nanocrystalline Si formation in SiO_x . In thermal annealing study, we have found the nanocrystalline Si formation threshold in terms of annealing times and temperatures. Nanocrystalline peak formation was detected by Raman spectroscopy. We have compared the threshold of samples C3, H7 and two sputtered samples (one with hydrogen and one without). We have observed an Arrhenius like relationship between the reaction rate, as represented by the threshold time to observe the nanocrystalline Si peak at a given temperature. Comparing sputtered samples, we observed that the threshold of hydrogenated sample is lower than the non-hydrogenated one. Therefore, we conclude that hydrogen lowers the threshold by decreasing the activation energy for the formation of nanocrystals. Laser density threshold energy for the formation of nanocrystals C3 and H7 is also lower than sputtered samples and threshold of H7 is lower than threshold of C3. ERDA results shows that hydrogen content of the films is in the following order: $\text{H} > \text{C} > \text{hydrogenated sputtered} > \text{non-hydrogenated sputtered}$, with the threshold for the formation nanocrystalline Si being the highest for the last samples in the order. This ordering of the samples with respect to their hydrogen content suggest that the threshold order may be attributed to the hydrogen content. We have done laser processing using an Ar-ion laser (488 nm) focused in a microscope and scanned the samples across the laser beam to obtain laser processed lines. For a fixed dwell time, we have scanned the samples by varying power density. Similar to the analysis done in the thermal annealing method, we have measured the thresholds for formation of nanocrystals by Raman scattering. We showed that the order of the samples with hydrogen content and their threshold times measured by two different methods are consistent with each other. We showed that the nanocrystal formation threshold also depends on the oxygen content. Up to 26 at.% oxygen concentration level in the samples, the threshold decreases. Higher oxygen content increased the threshold. Increasing oxygen concentration nanocrystalline peaks enhance the crystal quality measured from Raman peak frequency and linewidth. We also analyzed the Raman intensity spatially over the scanned lines. Dektak profilometry indicates that the scanned lines shrink

by 5 % and Raman peaks are observed on these shrunk zones. To sum up, we have analyzed the effect of composition, laser power density, annealing time and temperature on the nanocrystalline silicon formation.

Chapter 5

Conclusions and future work

We have fabricated silicon rich oxide thin films by PECVD and sputter deposition. For PECVD, three series was made by different combinations of process gases ($\text{SiH}_4\text{:H}_2\text{+N}_2\text{O}$, $\text{SiH}_4\text{:N}_2\text{+N}_2\text{O}$, $\text{SiH}_4\text{:H}_2\text{+CO}_2$). Within each series, N_2O and CO_2 flow rates were varied to obtain different films with different compositions.

We have analyzed the composition of thin films grown by PECVD and sputter deposition methods. For compositional analysis, the main method was Elastic Recoil Detection Analysis (ERDA), which is an ion-beam method for compositional analysis that is sensitive to light atoms like hydrogen. The ERDA results for all series were listed in table 3.3. We observed that silicon content decrease as the N_2O or CO_2 flow rates increase for PECVD samples. The hydrogen content was measured between 3 and 20 % for all films. Comparing the samples that have $(\text{O+N})/\text{Si}$ content close the 1 from each series, we observed that the hydrogen content order of the sample series is $\text{N} > \text{H} > \text{C} > \text{hydrogenated sputtered} > \text{non-hydrogenated sputtered}$. Oxygen to silicon ratios of the sputtered samples was found to be close to 1.

For compositional analysis, X-ray Photoelectron Spectroscopy (XPS) was also used, as an alternative to ERDA. We found that O/Si ratios from XPS are close to ERDA results. Due to the noise in ERDA data for nitrogen, N/Si ratios were noisy, however we observed a linear relationship between ERDA and XPS data for

this ratio. Therefore ratios of oxygen and nitrogen to silicon can be found from XPS. If only hydrogen content, which can not be measured by XPS, is known, overall content of our films can be found.

XPS is not sensitive to hydrogen, but hydrogen bonds are detectable by FTIR. We observe that central frequencies of Si-H wagging mode at 650 cm^{-1} , Si-H stretching mode at 2100 cm^{-1} and Si-N stretching mode at 3300 cm^{-1} are correlated to the hydrogen content of the films. Therefore it may be possible to extract the H/Si ratio from FTIR data. It is possible to measure O/Si ratio as well. We observed that Si-O-Si stretching mode at 1050 cm^{-1} is linearly correlated to O/Si ratio obtained from ERDA.

For thickness measurements, we used variable angle spectroscopic ellipsometry. From the thickness information, we calculated the growth rates of each PECVD grown samples. We measured the index of refraction and the extinction coefficients from ellipsometric data. A relationship between refractive indices and Si, O, N, and H content of the film was observed (figure 3.25).

For the formation of Si nanocrystals, we used two methods: thermal annealing and laser processing methods. Thermal annealing was done by a rapid thermal processing system under certain annealing temperatures and times. Laser processing was done by focusing a 488 nm Ar-ion laser beam on the samples. For the characterization of nanocrystallization, we used Raman spectroscopy. For a fixed annealing time we observed that higher temperatures resulted in a better crystalline quality, observed by the shift of the nanocrystalline Si peak towards 521 cm^{-1} . A similar trend was observed for laser processing. As the power density of the laser increased, the nanocrystalline Si peak shifted more towards 521 cm^{-1} . Raman peak widths also get narrower as the power density is increased. For both methods, we observed that hydrogen decrease the temperature or power density threshold for the formation nanocrystalline Si. We compared the H series samples that have different O/Si ratios. We observed that oxygen decrease the power density threshold for nanocrystalline Si formation, up to a certain level (25 % at. concentration). More oxygen than this level resulted in a increase of the

power density threshold. We compared the order of laser power density threshold for nanocrystalline Si formation to the time threshold for nanocrystalline Si formation in thermal annealing method. We found that the order of thresholds are consistent.

The silicon nanocrystals and silicon crystal networks that are sought after in this thesis can also be used as excitonic sources for exciton-plasmon interactions. Confined to very small dimensions, emission efficiency of Si nanocrystals become very high. As such they can be used on various plasmonic surfaces, such as flat metal surfaces, uniform gratings and Moire surfaces. The ease and availability of silicon nanocrystals can provide for the formation of efficient solid state efficient exciton-plasmon coupling which may eventually lead to the lasing of Si nanocrystals, a long sought dream.

For application of silicon rich oxides to solar cells, it is necessary to characterize its nanocrystalline structure further. We expect our films to have a sponge-like silicon nanocrystal network structure. Transmission electron microscopy of annealed films may provide this information. To confirm the percolated structure, I-V and photocurrent measurements can be done.

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Appendix A

Comsol Multiphysics Tutorial

In this section we will explain how to model heating of a thin film scanned by a laser beam. This is an introductory tutorial, yet the model is customizable. One can adjust the constants and materials to model similar systems. The version used here is Comsol 3.3a.

1. Run Comsol Multiphysics
2. In the Model Navigator select 3D for space dimensions, then select Application Modes⇒Comsol Multiphysics⇒Heat Transfer⇒Convection and Conduction⇒Transient Analysis, click OK to exit the Model Navigator.

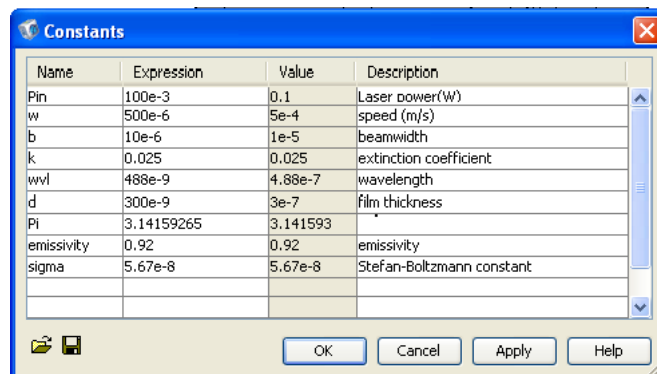


Figure A.1: Constants dialog box

3. In the Options⇒Constants dialog box enter the constant appropriately. (Figure A.1)
4. Select Draw⇒Work Plane Settings, in the dialog box select x-y plane z:0 and click OK. Now the screen will be showing the z=0 plane.
5. Select Draw⇒Specify Objects⇒Square. In the dialog box enter 3e-4. In the Base menu select Center. Click OK. (Figure A.2) This will create a 300 μm square in the z=0 plane. You may want to change the size depending on your application.

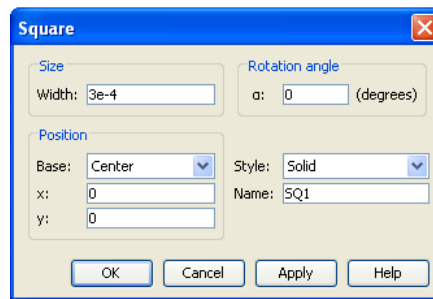


Figure A.2: Square dialog box

6. Select Options⇒Zoom⇒Zoom Extends. This will enlarge the square to fit the editor screen.
7. Select Draw⇒Specify Objects⇒Line. Fill in the dialog box as shown in figure A.3. This will create a line in the middle of the square.

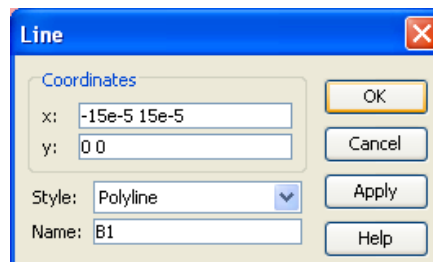


Figure A.3: Line dialog box

8. We want the mesh size on the line to be smaller than the rest of the shape. Select Mesh⇒Free Mesh Parameters. In the Global tab select Coarser in

the Predefined mesh sizes list. Then go to the Boundary tab and select 4 in the list. This boundary is the line in the middle and will turn to red now. Enter maximum element size 1e-6. Click OK.

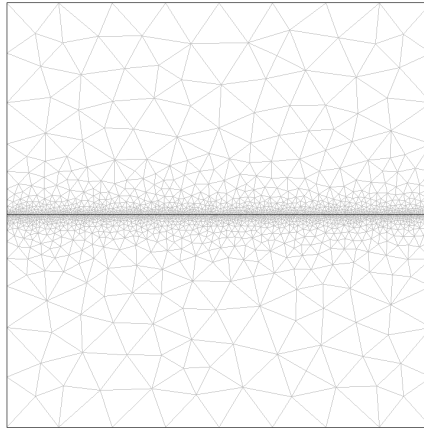


Figure A.4: Example mesh

9. Select Mesh⇒ Initialize Mesh. The resulted mesh should look like figure A.4
10. Until now, we worked on a 2D structure. Now we will extrude it to make a 3D structure. Select Mesh⇒ Extrude Mesh. In the geometry tab enter 1e-4 into Distance (Figure A.5). Go to the mesh tab and fill it as shown in figure A.6. Click OK. This will create a 100 μm thick structure and the mesh will be denser at the surface.

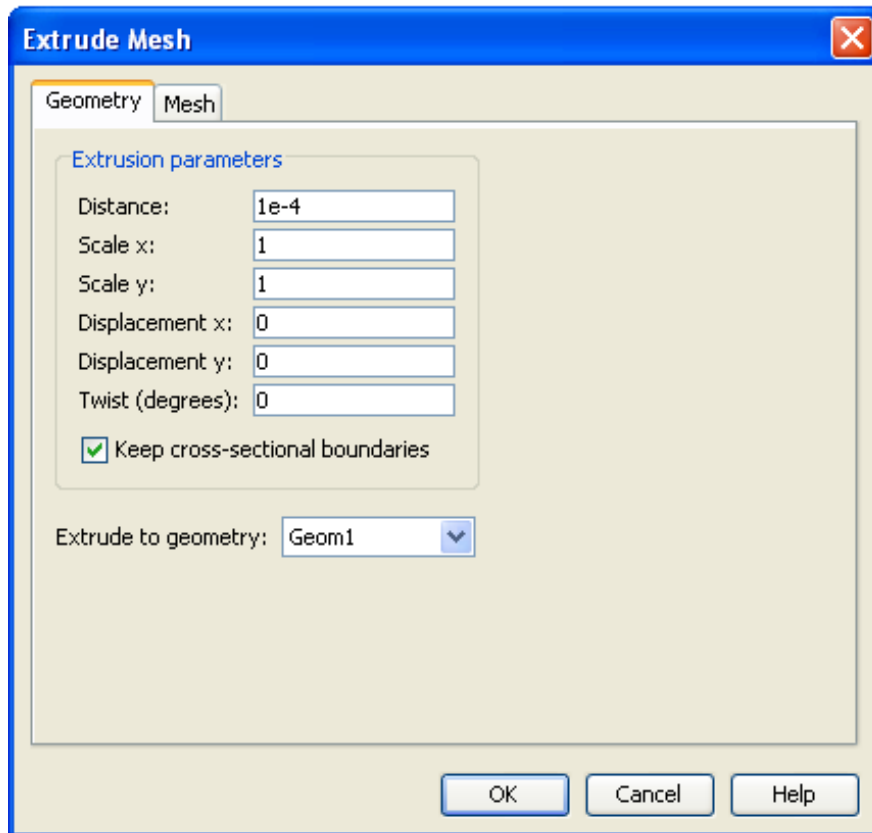


Figure A.5: Extrude Mesh dialog box

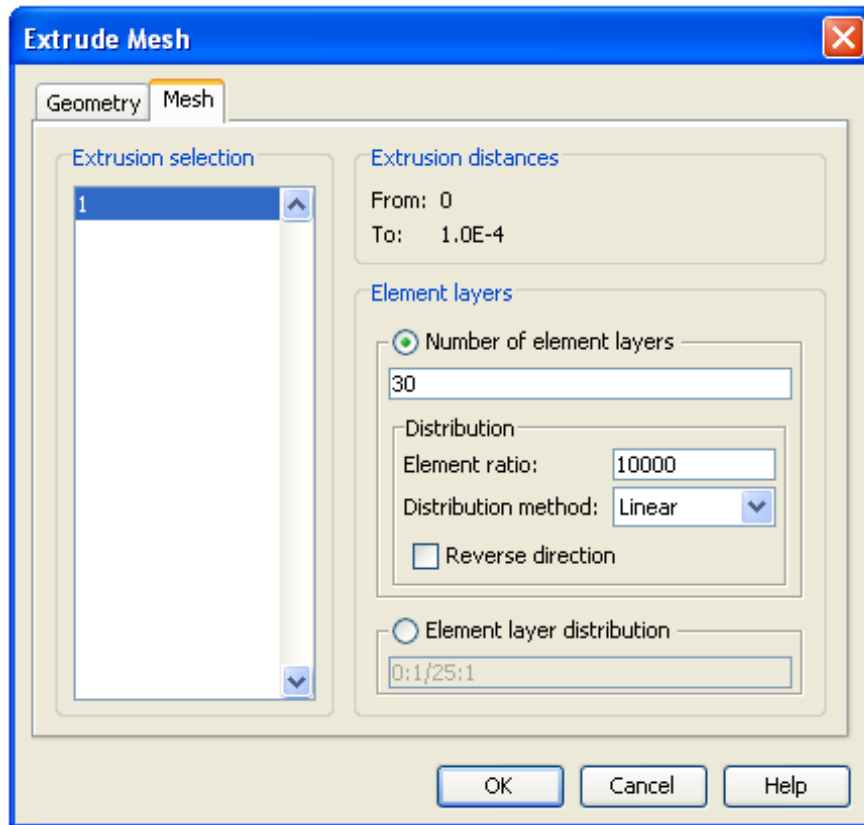


Figure A.6: Extrude Mesh dialog box

11. Now we have to define the materials. Select Physics⇒Subdomain Settings. Hold the CTRL button to select subdomains 1 and 2. Click load. Material/Coefficients Library will open. Under the Basic Material Properties select Silica Glass Click OK. (FigureA.7)

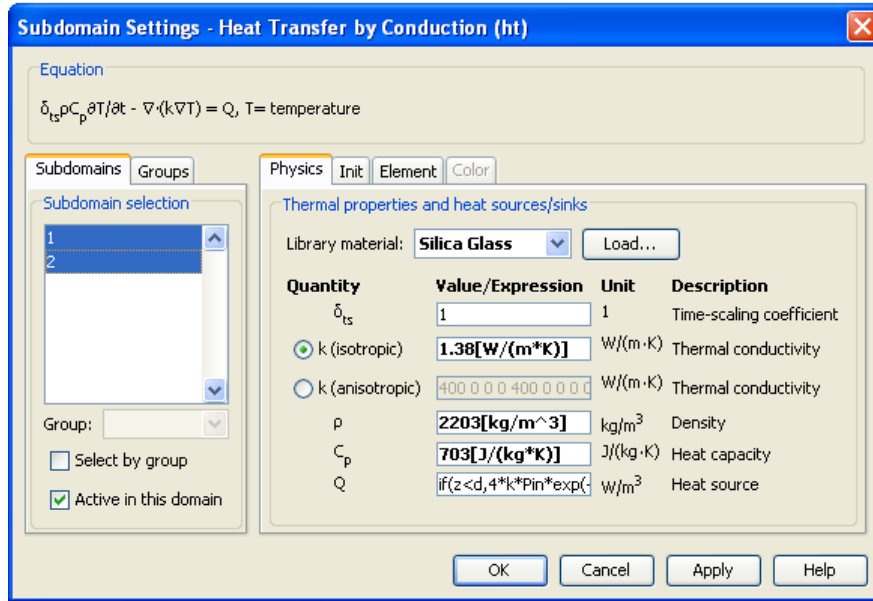


Figure A.7: Subdomain Settings dialog box

12. In the Subdomain Settings, we have to define heat source term as explained in the previous section. Enter the heat source term field the code below. This will define the heat source term only for the film area. Heat source term will be zero at the substrate. Figure (A.7)
13. In the Subdomain Settings, go to Init tab, select both 1 and 2, and enter 300 K into $T(t_0)$ field. This is the initial temperature. Click OK to exit Subdomain Settings dialog.

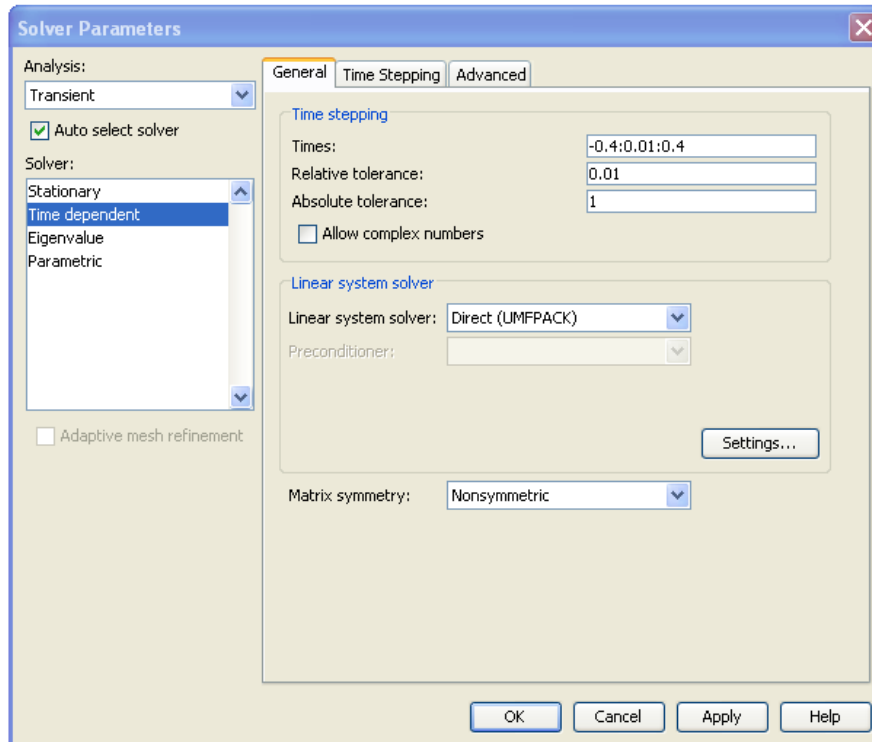


Figure A.8: Solver Parameters dialog box

14. Select Solve⇒Solver Parameters and fill in as shown in figure A.8.
15. Select Solve⇒Solve Problem.
16. Select Postprocessing⇒Plot Parameters then go to the General tab and select 0 in the solution at time list.
17. For cross section image, select Options⇒Suppress⇒Suppress Boundaries and select all boundaries except 6. Click OK. Select Postprocessing⇒Postprocessing Mode.
18. For temperature profile on the scanned line select Postprocessing⇒Domain Plot Parameters. Go to Line/Extrusion tab, click Line/Extrusion plot and select edge 8. Click OK. This will plot all the temperature profiles at the specified times. You may want to select a specific time from Domain Plot Parameters⇒General tab.