

The growth of microcrystalline thin films using ECR-PECVD:

Silicon and Silicon-Germanium

by

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Signatures have been redacted for privacy

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*to my better half, Kyu Sung Kim*

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## ABSTRACT

A high rate growth method of hydrogenated microcrystalline silicon,  $\mu\text{c-Si:H}$ , and silicon-germanium,  $\mu\text{c-(Si,Ge):H}$ , has been developed with very low hydrogen dilution ratio on foreign substrates, using a remote electron cyclotron resonance - plasma enhanced chemical vapor deposition (ECR-PECVD) process. In this work, the key variable was the hydrogen dilution, ratio of hydrogen to silane,  $[\text{H}_2]/[\text{SiH}_4]$ , which ranged from 3.3 to 10, adding helium systematically. Phase transition from amorphous to microcrystalline states was observed as the amount of added helium was varied. It has been found that hydrogenated microcrystalline silicon films with more than 70 % of crystalline volume fraction were formed at high growth rates of 3.2 Å/sec at low substrate temperature below 300 °C from the mixture of silane and hydrogen with a low hydrogen dilution ratio of as low as 3.3. The addition of helium did not increase the growth rate significantly, but it quickly served as disrupting microcrystalline formation. In addition, the substrate temperature-dependent phase transition was observed. The structural, electrical and optical properties, by Raman shift, x-ray diffraction, dark and photo conductivity, activation energy of dark conductivity, and photosensitivity measurements, were investigated to grow good quality  $\mu\text{c-Si:H}$  films at the low hydrogen dilution ratio with high growth rates. The prominent peaks at 520  $\text{cm}^{-1}$  from Raman Shift spectroscopy, crystalline peaks from x-ray diffraction pattern, small photosensitivity, and low activation energy of dark conductivity due to grain boundaries in microcrystalline silicon thin films indicated the characteristic of crystalline materials.

## CHAPTER 1. INTRODUCTION

### I. Overview

Silicon thin films have been successfully applied in various electronic devices, such as in thin film transistors (TFT), a switching device in flat panel liquid crystal displays (LCD), image sensors and photovoltaic solar cells, due to higher optical absorption than bulk crystalline silicon and efficient light trapping. The primary attribute of the technology is its large area capability by the plasma chemical vapor deposition (CVD) process on inexpensive substrates, for instance on glass, stainless steel, and plastic polyimide.

Hydrogenated amorphous silicon (a-Si:H) exhibits the full range of semiconducting properties of doping, photoconductivity, and junction formation, although with lower speed and current compared with single crystal silicon from its disordered nature. The plasma deposition technology along with the amorphous structure provide a wide set of compatible materials that allows diversity in device design and considerable band gap engineering.

Hydrogenated microcrystalline silicon ( $\mu\text{c-Si:H}$ ) thin films have received considerable interest due to their higher mobility and better frequency response than a-Si:H. They also do not suffer from light-induced degradation known for hydrogenated amorphous silicon (a-Si:H) [1]. Structural investigations of  $\mu\text{c-Si:H}$  [2, 3] show that the material consists of areas (grains) of perfect crystallinity with an average size of 20 nm forming larger columns parallel to the film growth axis and extending over the entire film thickness. Between these columns



there are disordered regions or internal voids, and the individual small "grains" are separated from each other only by crystalline imperfections like stacking faults.

The definitions for various morphologies of thin film silicon materials are as follows. An amorphous solid is in a non-equilibrium state of a material, which can take a variety of different macroscopic states depending upon the preparative process. It is a single amorphous phase with no feature size at all. Microcrystalline silicon is a mixture of amorphous and crystalline phases. The crystals with typical feature size of less than 20 nm are surrounded with grain boundaries, which are amorphous phase. Both a-Si:H and  $\mu\text{c-Si:H}$  have substantially different properties as compared to crystalline silicon. A thin film of hydrogenated silicon contains a large amount of hydrogen, which plays an essential role in the characteristics of such a material.

## II. Brief history of amorphous and microcrystalline silicon

N. F. Mott, the Nobel Prize recipient in Physics in 1977 for his work on "The Electron Theory of Disordered Systems", had already started his work on disordered systems in the 1930s with studies of the theory of liquid metals. P. W. Anderson, who shared the Nobel Prize with Mott, made important contribution to the world of amorphous semiconductors through his proposal of the model for localized levels [4].

Sterling and Swann, 1965 were the first to publish the formation of films of "silicon from silane" in a RF glow discharge. Soon after, the first low temperature microcrystalline silicon layers were deposited on glass substrates by Veprek and Marecek in 1968, who used hydrogen plasma and a chemical transport method at 600 °C. The first great breakthrough

came with the growth of amorphous silicon from silane ( $\text{SiH}_4$ ) plasma by Chittick et al. in 1969 [5]. They found that plasma-deposited a-Si had better photoconductive properties than that made by the evaporation and sputtering. The second major breakthrough was the 1975 discovery of the possibility of doping the material substitutionally by Spear and LeComber [6]. They demonstrated that the material can be doped n-type and p-type over a large range by adding phosphine ( $\text{PH}_3$ ) or diborane ( $\text{B}_2\text{H}_6$ ) to the plasma during growth and it is possible to control the position of the Fermi energy across most of the band gap. Although not clear at first, subsequent work by the Harvard and Chicago groups, showed that the improved properties were the result of hydrogen incorporation into the material [7, 8]. The hydrogen binds to dangling bond defects and removes the corresponding electronic states in the band gap, thus eliminating most of the trapping and recombination centers. Thus electronic-grade amorphous silicon is in fact an alloy of silicon and hydrogen, and was since then called hydrogenated amorphous silicon.

The first a-Si:H field effect transistor, announced in 1978 [9], had a silicon nitride gate dielectric, deposited in the same plasma reactor by combining the gases  $\text{SiH}_4$  and  $\text{NH}_3$ . The plasma nitride was an important innovation, which allowed these thin film transistors (TFT) to be fabricated on glass, at low temperature and with a very high on/off ratio. By this time it was realized that a great variety of silicon alloys could be fabricated by plasma deposition so that an extensive family of materials was available for the technology.

### III. Physics of hydrogenated amorphous and microcrystalline silicon

The silicon atoms are 4-fold coordinated in a tetrahedral bonding symmetry, but with a significant distribution in bond lengths and bond angles. The 5-10 atomic percent of hydrogen is bonded to the silicon atoms, mostly in the form of Si-H bonds, either isolated or on the surface of small voids. In a-Si:H, free electrons and holes have a scattering length of about interatomic spacing, and consequently a free carrier mobility of only about  $1 \text{ cm}^2/\text{Vs}$  compared to about  $100 \text{ cm}^2/\text{Vs}$  in poly-crystalline silicon. Most importantly, the disorder causes an exponential tail of localized states at the band edges extending into the forbidden gap. The energy dividing the extended and localized states is known as the mobility edge. The mobility gap separating the valence and conduction band mobility edges is approximately the optical band gap. Conduction of both electrons and holes occurs near the mobility edges, but involves frequent trapping and release from these localized states and consequently the effective carrier mobility is further reduced and is also thermally activated. The conduction band tail is narrower than the valence band tail, so that electrons ( $\sim 1 \text{ cm}^2/\text{Vs}$ ) have a higher mobility than holes ( $\sim 0.003 \text{ cm}^2/\text{Vs}$ ). Table 1.1 and Table 1.2 [10] show the criteria for 'device quality' amorphous and polycrystalline silicon films, respectively. Silicon-Germanium, (Si, Ge):H, alloys attract special interest due to their tuning ability of optical band gap from 1.0 to 1.7 eV, depending on the Ge content.

Table 1.1. Properties of 'device quality' amorphous silicon films.

<b>Property</b>	
AM 1.5 100mW/cm <sup>2</sup> photoconductivity	$1 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$
Dark conductivity	$1 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$
Photosensitivity (photo/dark conductivity)	$> 10^5$
Optical band gap	$\sim 1.7 \text{ eV}$
Activation energy of dark conductivity	$\sim 0.8 \text{ eV}$
Prominent peaks at Raman Shift	$480 \text{ cm}^{-1}$

Table 1.2. Properties of 'device quality' microcrystalline silicon films.

<b>Property</b>	
Orientation of the grains (XRD)	Predominantly (220)
AM 1.5 100mW/cm <sup>2</sup> photoconductivity	$1 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$
Dark Conductivity	$1 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$
Photosensitivity (photo/dark conductivity)	$< 10^2$
Band gap, indirect	1.0 - 1.1 eV
Activation energy of dark conductivity	$< 0.5 \text{ eV}$
Prominent peaks at Raman Shift	$480 \text{ cm}^{-1}$ and $520 \text{ cm}^{-1}$

## CHAPTER 2 SAMPLE PREPARATION

### I. Physics of plasma CVD

A *plasma* can be defined as a partially ionized, quasineutral gas. If the very low number of charged particles, ions and electrons, existing in any gas at any temperature is increased by an external source, the electric field due to charge separation can become strong enough to limit particles' own motion and maintain the macroscopic neutrality. This ionized gas is called plasma. The plasma deposition is characterized by the use of non-equilibrium plasma (low-temperature plasma), which forms a non-equilibrium gas phase, which is substantially different from usual thermal CVD method. The electron energy in a plasma is 1-10 eV, which corresponds to  $10^4$  -  $10^5$  K in the electron temperature,  $T_e$ , the translational temperature,  $T_{\text{gas}}$ , of the gas molecules (or atoms),  $\sim 500\text{K}$ , is close to the temperature of the apparatus (the normal temperature), therefore the ratio of  $T_e$  to  $T_{\text{gas}}$  is between  $10^2$  and  $10^3$  K. However, because of their large mass, neutrals and ions in the plasma have low energy ( a few hundredth of eV). Under these nonequilibrium conditions, the initiation of chemical reactions occurs by collisions with the "hot" electrons. This allows the processing temperature to be much lower than in conventional thermal process using similar chemistry.

The kinetic energy of the electron is responsible for the decomposition of the molecule. By collision with an electron, a molecule is activated to a higher energy state, and its dissociation or ionization then takes place. If  $\text{B}_2\text{H}_6$  or  $\text{PH}_3$  is mixed with the source gas  $\text{SiH}_4$

in the plasma process, boron or P can be easily doped into a-Si:H, without requiring any diffusion of B or P at higher temperature.

## II. Remote ECR-PECVD system at MRC in Iowa State University

Figure 2.1. shows the schematic illustration of the remote electron cyclotron resonance plasma enhanced chemical vapor deposition system at Microelectronics Research Center in Iowa State University. The ECR reactor consists of a two-zone reactor, in which the intense plasma zone is separated from the substrate. The  $\text{SiH}_4$  and  $\text{GeH}_4$  are excited at a different location from the plasma, which is generated in a carrier gas such as hydrogen and helium by microwave excitation with 2.45 GHz in a remote chamber. The condition of electron cyclotron resonance (ECR) is achieved when the microwave angular frequency  $\omega$  matches the electron cyclotron frequency,  $\omega = eB/m$ . Therefore, for a given frequency, the required magnetic field is  $B = \omega m/e$ , which corresponds to 880 G for  $\omega/2\pi = 2.45$  GHz. The remote plasma chamber acts as a resonance cavity. The plasma absorbs more than 70 % of the microwave power. The microwave power required to sustain stable plasma is reduced by one-order of magnitude with respect to non-magnetically confined plasma.

The electron density for ECR-CVD is high compared with those of a conventional RF glow discharge. The minimum gas pressure allowing the generation of plasma is much lower under ECR conditions than conventional RF discharge, because the threshold pressure strongly decrease, by almost an order of magnitude, as the magnetic field approaches the ECR condition, since the electrons have a long mean free path as they rotate around the field.

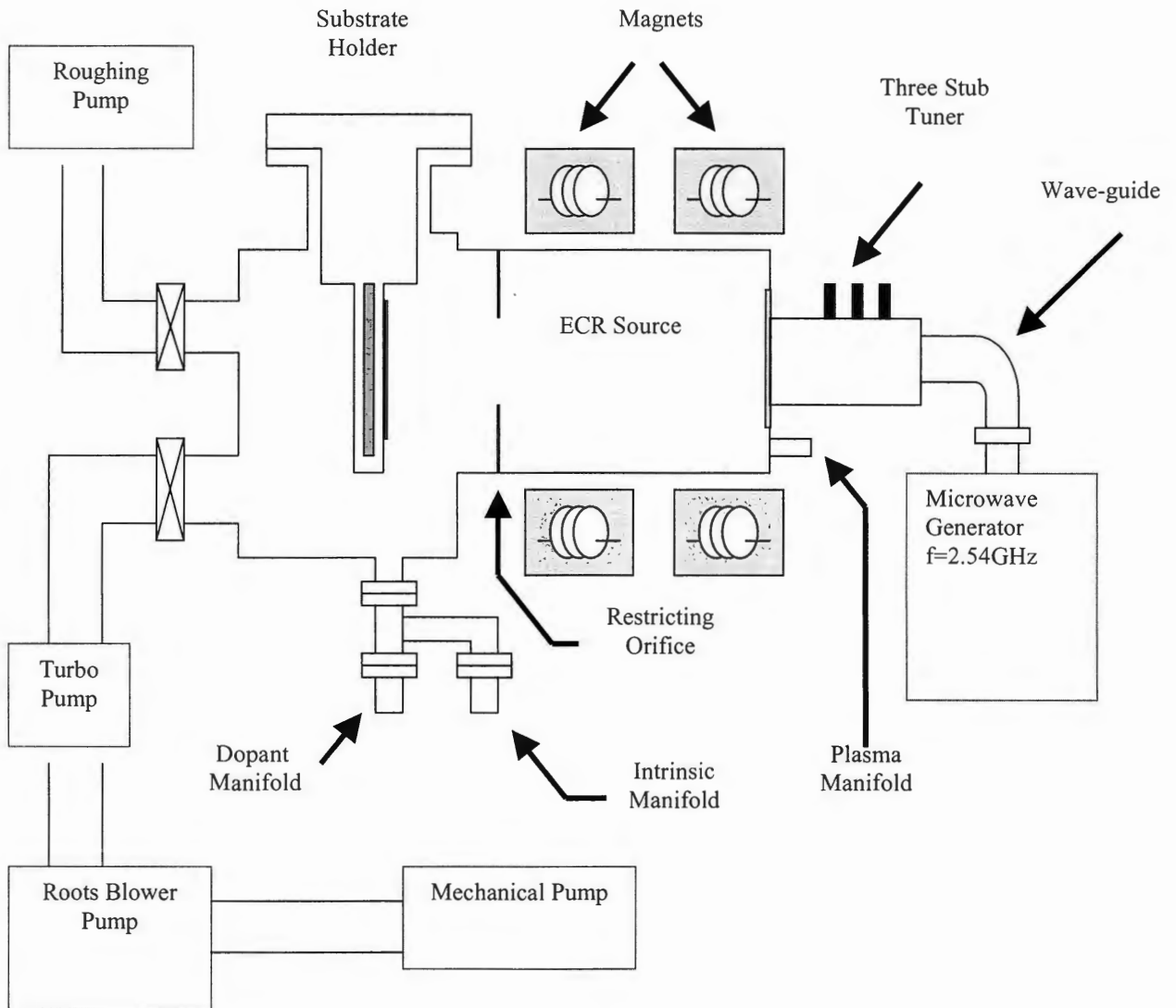


Figure 2.1. ECR-PECVD system in MRC at Iowa State University.

The advantage of the ECR microwave remote plasma CVD compared to conventional glow discharge are (1) the plasma is generated at low pressures, and (2) is remote from the substrate. Low pressure prevents gas phase polymerization and the generation of higher order radicals (such as poly silanes) and the remote plasma zone allows for a good control over ion and radical flux arriving at the substrate. And the other advantages are (3) Efficient energy transfer from the microwave field to the plasma; (4) Easy control of the ion energy by the gas pressure to avoid high-energy particle bombardment of the growing films. Thereby it produces less stress in the film and less damage to the growing surface; (5) Better control of the dissociation of the deposition gas; (6) Reduced powered electrode effects, such as contamination, self-biasing, and hot electron generation; (7) High ionization density; and (8) High plasma density.

### III. Experiment

The plasma was generated in the remote chamber from substrate by microwave excitation at 2.54 GHz through a quartz window. A rectangular waveguide system was used to transport the microwaves to the chamber. The system has three tuners to tune the polarization of the microwaves. The ECR condition was established with the use of two external magnetic coils. By adjusting the magnetic field strength of each coil, the position and strength of ECR region within the plasma generation region can be controlled. Two DC power supplies are used to power the coils. The reflected power from the substrate was set to be slightly above the minimum value possible. This setting corresponds to a maximum power transfer from the source to plasma and again to substrate, as well as stable magnetic field at



the position of active plasma. The restricting orifice, which divides ECR chamber and deposition chamber, provides uniformity and diverging cone shape of the plasma entering the deposition chamber. The substrate holder uses a stainless steel mask to hold the substrate in place. Typical substrate sizes are  $2 \times 2$  in<sup>2</sup>. Throughout this research, 7059 corning glasses are used for substrates. The substrate holder is externally attached to a heating block, which can control the substrate temperature up to 800 °C. The process chambers are evacuated by the turbopump down to  $10^{-6}$  to  $10^{-7}$  Torr before the deposition. The turbopump is backed by the roots blower pump and mechanical pump and the valves are open only after a separately located roughing pump brings the pressure down to  $\sim 1$  mTorr from atmospheric pressure. All pump systems are constantly purged with nitrogen to prevent building up of any residual toxic gases. There are three separate feedstock lines for plasma, intrinsic and dopant manifolds. Plasma gases of hydrogen and helium are introduced in the far end of the plasma source chamber. Plasma is generated by microwave excitation. The process gases, such as silane and germane, are flowed into the deposition chamber near the substrate. These gases are then ionized and dissociated into radicals due to the electrons with high energy by external magnetic field.

The substrates are prepared by boiling in acetone for 10 minutes, followed by 10 minutes of boiling in methanol. They are, then, stored in clean methanol. The substrate is blown dry with nitrogen just before being loaded. More than ten times of purging cycles is followed with nitrogen, plasma gas and deposition gas subsequently right after loading new substrate to remove any remnant moisture and oxygen gas. In between purges, the substrate heater is turned on and temperature is set about 50 °C higher than the desired deposition temperature to ensure full outgasing from the substrate. Following the purges, a shutter is

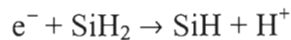
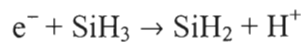
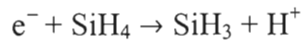
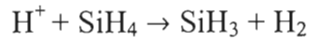
placed in front of the substrate for the chamber etching and dummy layer growth. He plasma is used for etching and growth of dummy layer on the chamber wall. The pressure is set to be 15 mTorr. This step is to remove any impurities that might be deposited from the previous experiment. Silane gas flows into chamber for etching as well as coating fresh dummy layer around the chamber. Microwave power is set at 150 W for these procedures. The deposition pressure for target material in this research is set between 5 and 10 mTorr. Microwave power was set at 200 W during film deposition. Upon completion of the deposition, the film is left to cool down to below 100 °C before being pulled out. While cooling, the chamber is back filled with 1 Torr of hydrogen and silane to prevent oxidation.

## CHAPTER 3 MATERIALS AND CHARACTERIZATION

### I. Growth mechanism of hydrogenated silicon thin films

The silane is introduced at a location near the substrate. As the magnetic field diverges into the deposition chamber, an electric field is generated in the plasma column, and ionized radicals ( $\text{SiH}_n^+$ ) from the plasma are driven to the substrate where they bombard the growing surface. A large ion flux with a sufficiently low energy enhances the deposition rate while material quality is preserved. The large ion flux allows the use of a low substrate temperature. The ion energy can be controlled by the gas pressure.

In the ECR-PECVD system, there are several reactions near the surface of substrate:



This dissociation occurs in the same way as in  $\text{GeH}_4$ . It is believed that  $\text{SiH}_3$  and  $\text{GeH}_3$  are dominant and the most important radicals, due to their higher surface mobility and low sticky coefficient. If other radicals become dominant during deposition, the surface will be rough and many dangling bonds and microvoids will be formed [11].

The standard model of hydrogen silicon growth by Matsuda, Gallagher and Perrin (MGP model) [12, 13, 14] showed that the growth of hydrogenated silicon film is limited

primarily by surface diffusion of  $\text{SiH}_3$  radical. The dangling bonds at the surface of a-Si:H are almost all bonded with H, with only an occasional bond being open to insertion by a silyl ( $\text{SiH}_3$ ) radical. When adjacent surface sites have silyl radicals bonded into them, the wing-bonded H atoms on adjacent sites self react, giving rise to  $\text{H}_2$ , and then eliminated from surface. This is possible because the bond energy of  $\text{H}_2$  is higher than the bond energy of Si-H. The resulting adjacent Si dangling bonds then react to create a Si lattice with a surface bonded H. This theory was improved later by Dalal and coworkers [15], who suggested that the primary consideration which determines the growth of hydrogenated silicon films is not surface diffusion, but rather the removal of surface hydrogen, and this elimination takes place not by reactions between neighboring H bonded to adjacent Si atoms, but rather by extraction of hydrogen by H radicals and inert gas ions. A high H dilution leads to a significant concentration of H ions and radicals impinging on the surface, and these remove the bonded H. The H ions also penetrate deeper into the lattice, and remove some more bulk H ions. The role of inert gas ions, such as Ar and He is to break the surface H bonds, thereby creating a dangling bond, and allowing another silyl radical to insert itself. The inert gas ions do not penetrate deep into the substrate, but H ions do. If the surface hydrogen is not removed, then the bonded Si-H structures get buried, new material grows around it, and a microstructure with a significant void concentration and clustered Si-H bonds form in the lattice. Such microstructure then leads to rapid degradation. Bombardment by inert gas ions can enhance the elimination of excess H at the surface, thereby reducing the probability of forming microvoids in the films. High ion flux densities are beneficial, but high energies, in excess of  $\sim 10$  eV or so may damage the material. We only need a few eV ions ( $\sim 3$  eV) to break the Si-H bonds at the surface [16].

## II. The phase diagram of hydrogenated microcrystalline silicon films

The role of H dilution is complex. It removes H from the surface and subsurface, enhances radical selectivity by increasing the fraction of silyl radicals in the growth process [17], and is also involved in subsurface bond reconstruction (Etching). H ions can convert a-Si into microcrystalline Si [18]. In contrast, when H ions are not present, or the ion energy is low ( $<1$  eV), the material is highly defective, and a very high temperature ( $\sim 450$  °C) must be used to obtain satisfactory properties. H ions with enough energy ( $>2-3$  eV) to break the surface-bonded H and penetrate the lattice to homogenize and improve the microstructure by removing weakly bonded H, are essential for promoting the growth of better materials.

It is generally accepted in  $\mu\text{c-Si:H}$  community that the amorphous-to-microcrystalline silicon transition is favored in highly H diluted silane discharge at high power density or in sequential alternative discharges of  $\text{SiH}_4$  and  $\text{H}_2$  gases [19, 20]. When  $\mu\text{c-Si:H}$  is deposited on noncrystalline substrates at low substrate temperature ( $< 500^\circ\text{C}$ ) the layer usually grows amorphous at first and a so-called incubation layer is formed, in which the crystallites start to nucleate [21]. As the deposition goes on, the silicon crystallites enlarge and aggregate until the transition is complete [22]. Depending on the deposition conditions the thickness of the transition layer ranges from several nanometers up to a few hundred nanometers [23].

The electronic defects are supposed to be concentrated at boundaries between the crystalline grains [24]. Seto introduced the grain boundary-trapping model [25], where in polycrystalline silicon the transport properties are governed by carrier trapping at the boundaries, leading to the creation of potential energy barriers, which impede the motion of carriers between grains. However, in relatively small grains of about 10nm, the number of

free carriers is not sufficient to completely fill the grain boundary defects and build up the barriers at the grain boundaries [26, 27]. Yet many impurities, in particular oxygen contamination [28], can introduce additional carriers and give rise to grain boundary barriers. On the other hand, the grain boundaries can be passivated by a high concentration of hydrogen [29].

Among the most important contributions for the understanding of the physical and chemical processes in the plasma deposition of the  $\mu\text{c-Si:H}$  materials have been the work of Veprek, who was the first to recognize that the low-pressure plasma deposition is in fact the result of a competition between "deposition" and "etching" by the reactive species in the plasma [30]. For a gas flow of almost pure silane in low-pressure plasma, the dominant process is the deposition of silicon hydrides that produce a film of hydrogenated amorphous silicon, as the small concentration of active radicals in the plasma provides a negligible etching of the surface. Veprek showed that when the rate of etching, mostly due to the large amount of hydrogen, becomes of the same order as that of the deposition of silicon, it is favorable for the formation of the crystalline silicon films. High rate of chemical exchange between the solid and the plasma will yield a quasi-equilibrium situation that will facilitate the formation of the thermodynamically stable material.

Recently, there have been serious discussions on the existence of phase transition from amorphous to microcrystalline phases in the functions of hydrogen dilution to silane ( $[\text{H}_2/\text{SiH}_4]$ ). The high dilution of silane with hydrogen was found to enhance the crystallization of PECVD Si films [31]. Therefore, hydrogen atoms are believed to promote surface coverage effect, the etching reaction, and/or the modification of the Si-Si network. The use of highly diluted silane also gives rise to a high hydrogen atom flux toward the

surfaces and also that it favors the production of silyl ( $\text{SiH}_3$ ) radicals that are supposed to be the main film precursor [32]. Fujiwara and coworkers showed that a  $\mu\text{c-Si:H}$  nuclei density increases significantly as the hydrogen dilution ratio to silane increases [33].

One of the most important results from highly diluted hydrogen in plasma is the effective etching mechanism. Therefore, it becomes general agreement that removal of hydrogen from the growth surface during growth of silicon film is the key factor to observe the transition from amorphous to microcrystalline phases. The consensus in the community is that  $\mu\text{c-Si:H}$  films are to be deposited under the condition of  $[\text{H}_2/\text{SiH}_4] > 100$  [34]. The most recent comprehensive study by J. Koh on the phase diagram of  $\mu\text{c-Si:H}$  shows that, to ensure crystalline volume fraction of above 70 %, it is required at least to have  $[\text{H}_2/\text{SiH}_4] > 40$  [35].

The questions to be answered are as follows. (1) What is the minimum amount of hydrogen dilution to have phase transition from amorphous to microcrystalline silicon films of about  $1\mu\text{m}$  thickness? (2) What is the effect of adding He ions, possessing energies of  $\sim 10$  eV, to phase transition and (3) to growth rates? (4) Is there any substrate temperature-dependent phase transition? (5) What would it be the growth rate for  $\mu\text{c-Si:H}$  grown by ECR-PECVD? These questions are the primary motivations throughout this investigation.

### III. Characterization of hydrogenated microcrystalline silicon films

The Raman Shift spectra, x-ray diffraction, photo- and dark- conductivity, and activation energy of dark conductivity measurements were conducted to investigate microcrystalline characteristics of plasma deposited silicon films. The thickness  $t$  of films are obtained from the measurements of transmission scan in the wavelength range of 1000 to

2500 nm using Lambda-9 spectrophotometer as shown in Figure 3.1. The relationship to calculate the thickness is  $t = 1 / [2 n (1/\lambda_1 - 1/\lambda_2)]$ , where  $n$  is index of reflection and  $\lambda$ s are wavelengths of adjacent peaks. Conductivity measurements provide the early insight to the structural and electrical qualities. The photoconductivity is measured under illumination of 1.5 AMS lamp with a spectrum similar to the Sun. A 100 V is applied across the film and the current is measured. The conductivities are given by  $\sigma = (I/V) (W/Lt)$ , where  $W/L$  is the ratio of width to length at contact points, and  $t$  is the thickness of film. The characteristic of microcrystalline silicon is its higher dark conductivity than amorphous silicon. Amorphous silicon will have dark conductivities of between  $10^{-9}$  to  $10^{-11} \Omega^{-1} \text{ cm}^{-1}$ , while microcrystalline silicon will have in the  $10^{-3}$  to  $10^{-5} \Omega^{-1} \text{ cm}^{-1}$ . The photosensitivity is the ratio of photoconductivity to dark conductivity. The good quality amorphous silicon will have photosensitivity more than  $10^5$ , while good quality microcrystalline silicon film will have less than  $10^2$ . Prior to the temperature-dependent conductivity measurements the films are annealed at 200 °C for at least 1 hour followed by quenching to room temperature. Then the dark conductivity was measured as the films was cooled with a rate  $dT/dt = 10 \text{ K}/10 \text{ min}$ . In Figure 3.2., for the temperature range between 200 °C and 100 °C, Arrhenius plots of dark conductivity shows activated behavior  $\sigma = \sigma_0 \exp(-E_A/kT)$ , with an activation energy of  $E_A$ . For amorphous silicon film, the activation energy is  $\sim 0.8 \text{ eV}$  and it is roughly a half of the cubic band gap. It is expected to have less than 0.5 eV of activation energy for the microcrystalline with grain boundaries.

X-ray peaks are measured using Cu  $K\alpha$  line ( $\lambda=1.542 \text{ \AA}$ ) with step size of  $0.05^\circ$  of  $2\theta$ . Microcrystalline silicon film will show prominent peaks from the (111), (220), and (311) planes at  $28.1^\circ$ ,  $47.2^\circ$ , and  $55.5^\circ$ , respectively. The average grain size in the microcrystalline



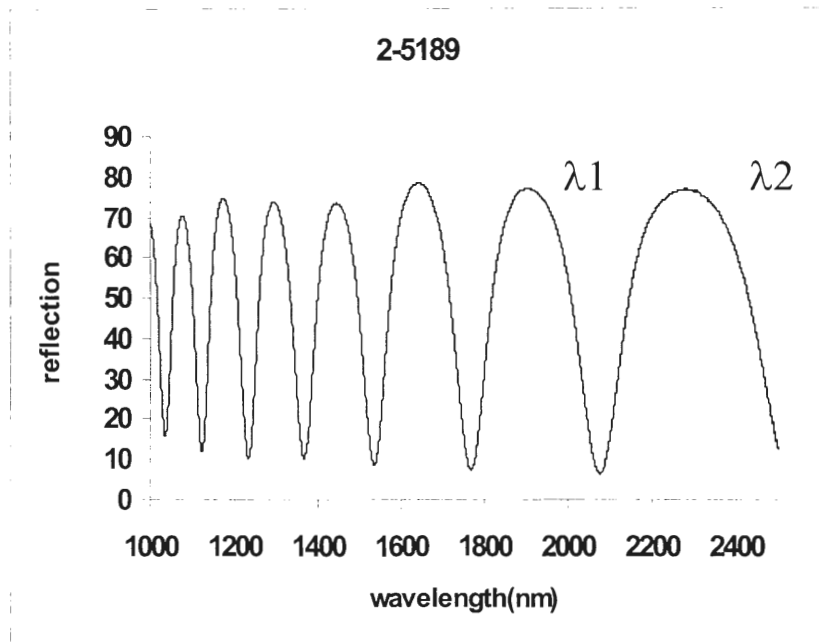


Figure 3.1. The thickness measurement using Lambda-9.

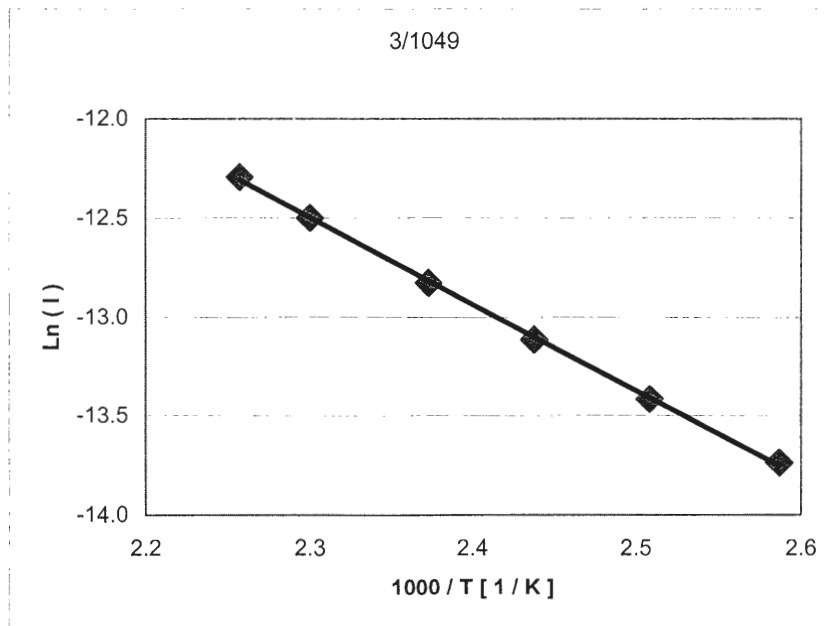


Figure 3.2. The measurement of activation energy of dark conductivity.

films can be estimated using Scherrer's formula,  $x = 0.94 \lambda / (B_{2\theta} \cos\theta_B)$ , where  $B_{2\theta}$  is fullwidth in radians at Half maximum intensity, if film is thick enough compared to the wavelength of the x-ray. The Raman spectroscopy measures energy shift of the emitted light from the incoming light energy by either gaining or losing energy by interacting with phonons and it is the best method to determine the phases present in silicon films. Raman Shift spectra (Nd:YAG Laser with  $\lambda=1064$  nm) have been used to measure the structure changes of the films, in which the peaks at  $520 \text{ cm}^{-1}$  are associated with the transverse optical (TO) mode of crystal silicon, whereas signals of the amorphous silicon with grain boundaries appear between  $480 \text{ cm}^{-1}$  and  $520 \text{ cm}^{-2}$  [36]. The crystalline volume fraction  $V_f$ , is defined from the deconvoluted intensities  $I_c$  and  $I_a$  of the Raman spectra, at  $520 \text{ cm}^{-1}$  and  $480 - 520 \text{ cm}^{-2}$ , respectively, by applying  $V_f = I_c / (I_c + I_a)$ .

## CHAPTER 4 RESULTS AND DISCUSSION

A set of thirteen films were prepared to investigate; firstly, the effect of hydrogen dilution as the ratio of hydrogen to silane varies from 10 to 3.3, and secondly, the effect of adding He ion systematically to plasma. Deposition time (60 min), substrate temperature (350 °C), deposition pressure (5 mTorr), and microwave power (200 W) were set constant. Samples were divided into three groups and labeled as He = 0 sccm, He = 14 sccm, and He = 28 sccm groups. The deposition parameters are shown in Table 4.1, 4.2 and 4.3, respectively.

Figure 4.1. shows a typical Raman Shift spectra. Intensity in arbitrary unit vs. Raman Shift is plotted in a range within 440 and 600  $\text{cm}^{-1}$  to identify a crystalline peak and a peak from amorphous silicon with grain boundaries. Crystalline volume fraction is derived from  $V_f = I_c/(I_c+I_a)$ , where  $I_c$  and  $I_a$  are peak intensities from crystalline and amorphous, respectively.

In Figure 4.2, Raman spectra of the group of He = 0 sccm are plotted. Peaks are off-set along x-axis for better view. It is clear that microcrystalline silicon formed from the peak at 520  $\text{cm}^{-1}$  and broad shoulders near 480  $\text{cm}^{-1}$  indicate that mixed phases are present in these films. The activation energies are added for comparison with the Raman result. The low activation energy confirms that it is microcrystalline silicon film. There is no indication of abrupt change as hydrogen dilution decreases from 10 down to 3.3. This is the main result in this research, i.e., microcrystalline phase can be formed with hydrogen dilution as low as 3.3.

Table 4.1. Deposition parameters for He = 0 sccm group.

Sample #	H <sub>2</sub> [sccm]	He [sccm]	SiH <sub>4</sub> [sccm]	H <sub>2</sub> / SiH <sub>4</sub>
980	20	0	6	3.3
981	30	0	6	5.0
982	40	0	6	6.7
983	50	0	6	8.3
984	60	0	6	10.0

Table 4.2. Deposition parameters for He = 14 sccm group.

Sample #	H <sub>2</sub> [sccm]	He [sccm]	SiH <sub>4</sub> [sccm]	H <sub>2</sub> / SiH <sub>4</sub>
985	20	14	6	3.3
986	30	14	6	5.0
988	40	14	6	6.7
989	50	14	6	8.3
990	60	14	6	10.0

Table 4.3. Deposition parameters for He = 28 sccm group.

Sample #	H <sub>2</sub> [sccm]	He [sccm]	SiH <sub>4</sub> [sccm]	H <sub>2</sub> / SiH <sub>4</sub>
992	20	28	6	3.3
994	30	28	6	5.0
993	40	28	6	6.7

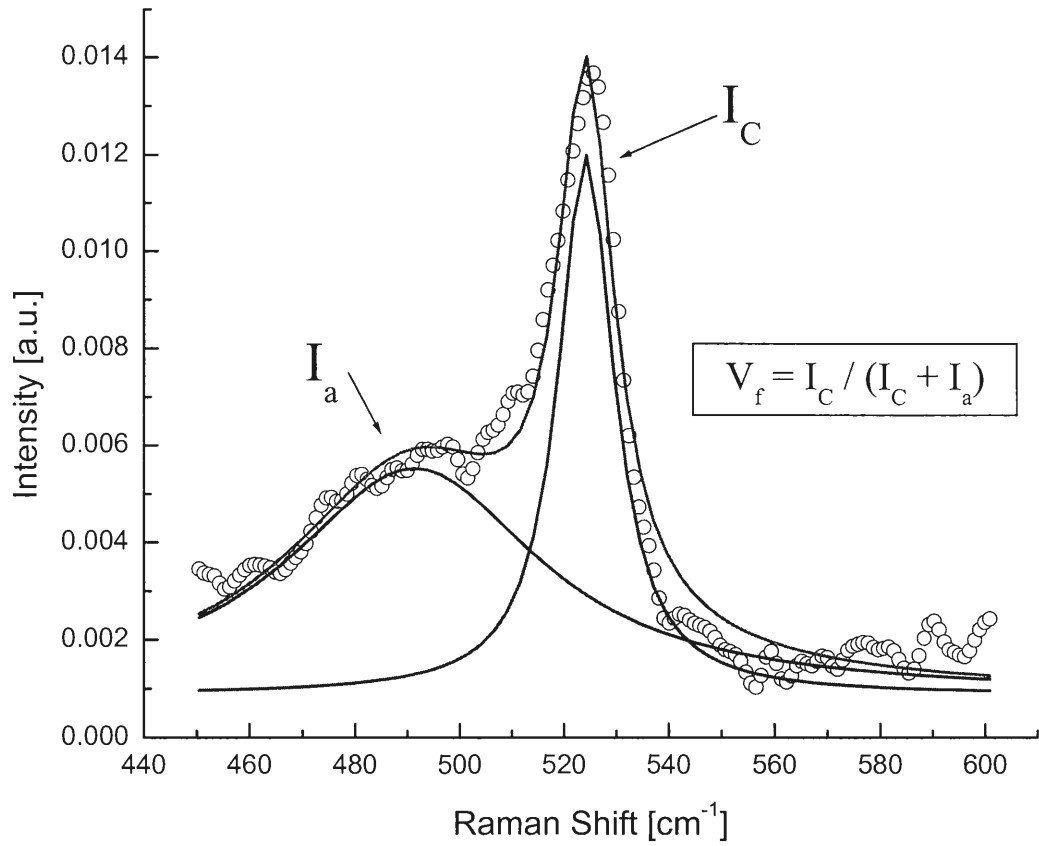


Figure 4.1. Deconvolution into two Lorentzian curves. The  $V_f$  is crystalline volume fraction.

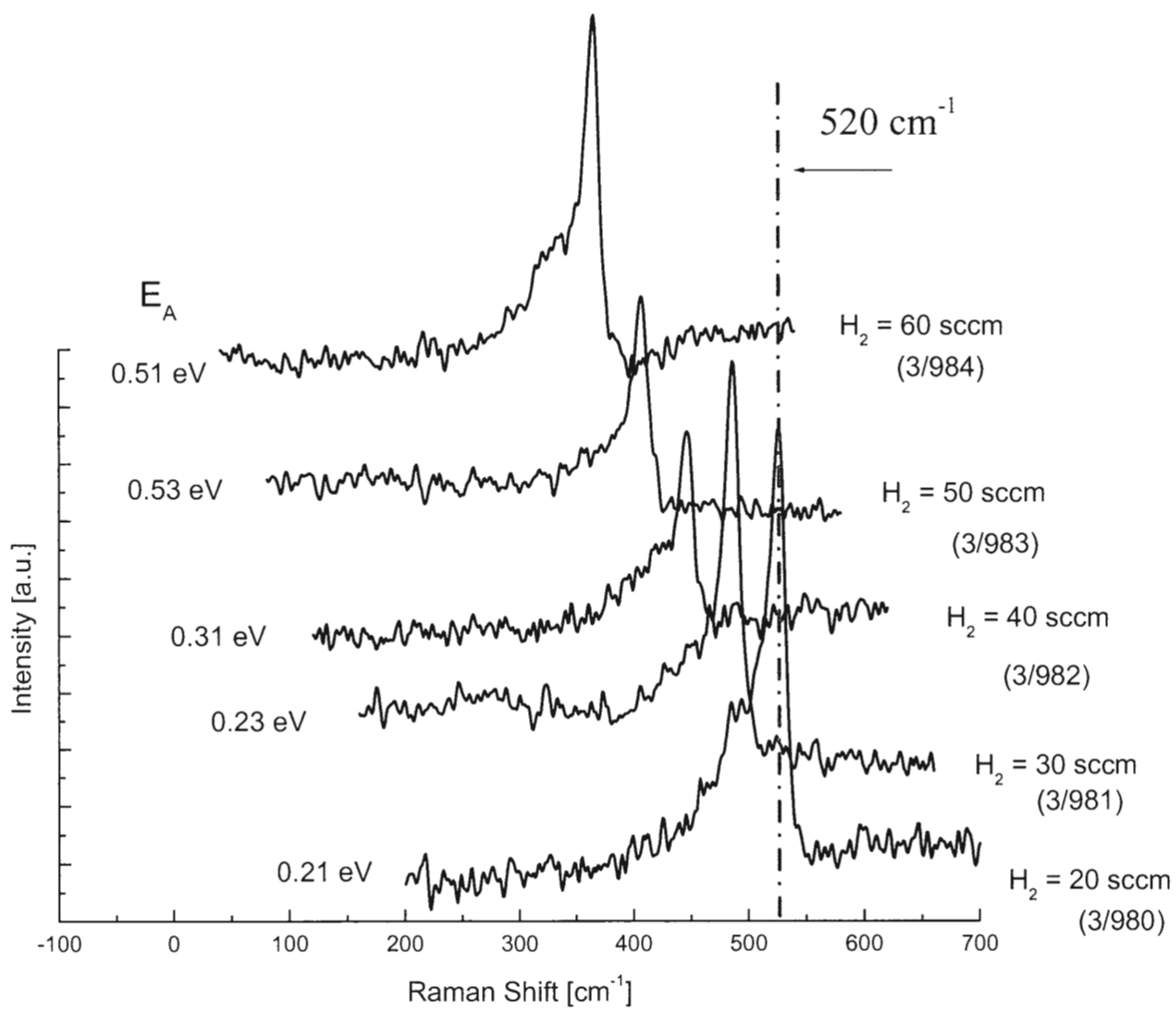


Figure 4.2 Raman spectra of He = 0 sccm. Peaks are off-set for better view.

To investigate the effect of adding inert ion into plasma, helium is added systematically. Figure 4.3 and Figure 4.4 are Raman Shift spectra plots of He = 14 sccm and He = 28 sccm groups, respectively. Activation energy hiked up as microcrystalline phase faded away as a result of He addition in a gradual manner.

Two important results were obtained by adding helium. First, films grown with higher hydrogen dilution failed to make transition to microcrystalline phase. Second, as the flow rate of helium doubled, microcrystalline phase stopped forming more quickly as hydrogen dilution decreased. However, microcrystalline phase was still formed for low hydrogen dilution, although microcrystalline phase for highly diluted hydrogen samples disappeared readily. This is quite interesting because this means that helium ion in plasma, with energy of  $\sim 10$  eV, is too energetic for microcrystalline formation. Bombardment of He ions on the growth surface would destroy the thermodynamically equilibrium state, which is a necessary stage for the formation of microcrystalline phase. Furthermore, the deposition growth rate was not significantly affected by adding helium. For example, films grown with 20 sccm of hydrogen for three groups resulted in the growth rate of 3.24, 3.36, and 3.38 Å/sec, respectively. This indicates that the growth mechanism of amorphous and microcrystalline phases is quite different from each other. In amorphous silicon growth, adding helium gives rise to higher growth rate. The growth of microcrystalline phase involves very slow chemical mechanism. There must be present a certain amount of hydrogen for subsurface etching mechanism to remove microvoids and to passivate dangling Si bonds and growth surface requires to maintain an equilibrium state for transition to microcrystalline phase. Table 4.4, 4.5, and 4.6 is lists of film thickness, growth rate, photosensitivity, activation energy, identification of microcrystallinity and volume fraction from Raman Shift spectra.

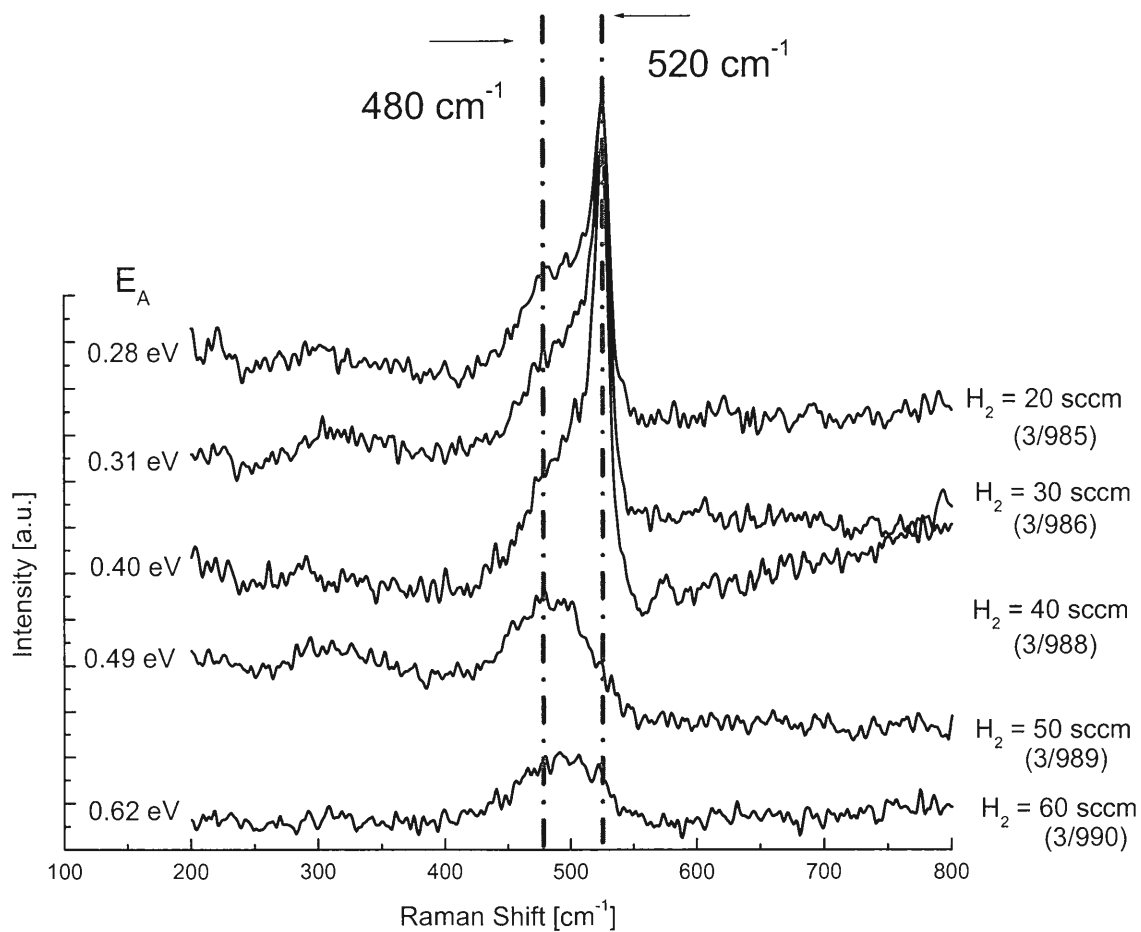


Figure 4.3. Raman spectra of He = 14 sccm.



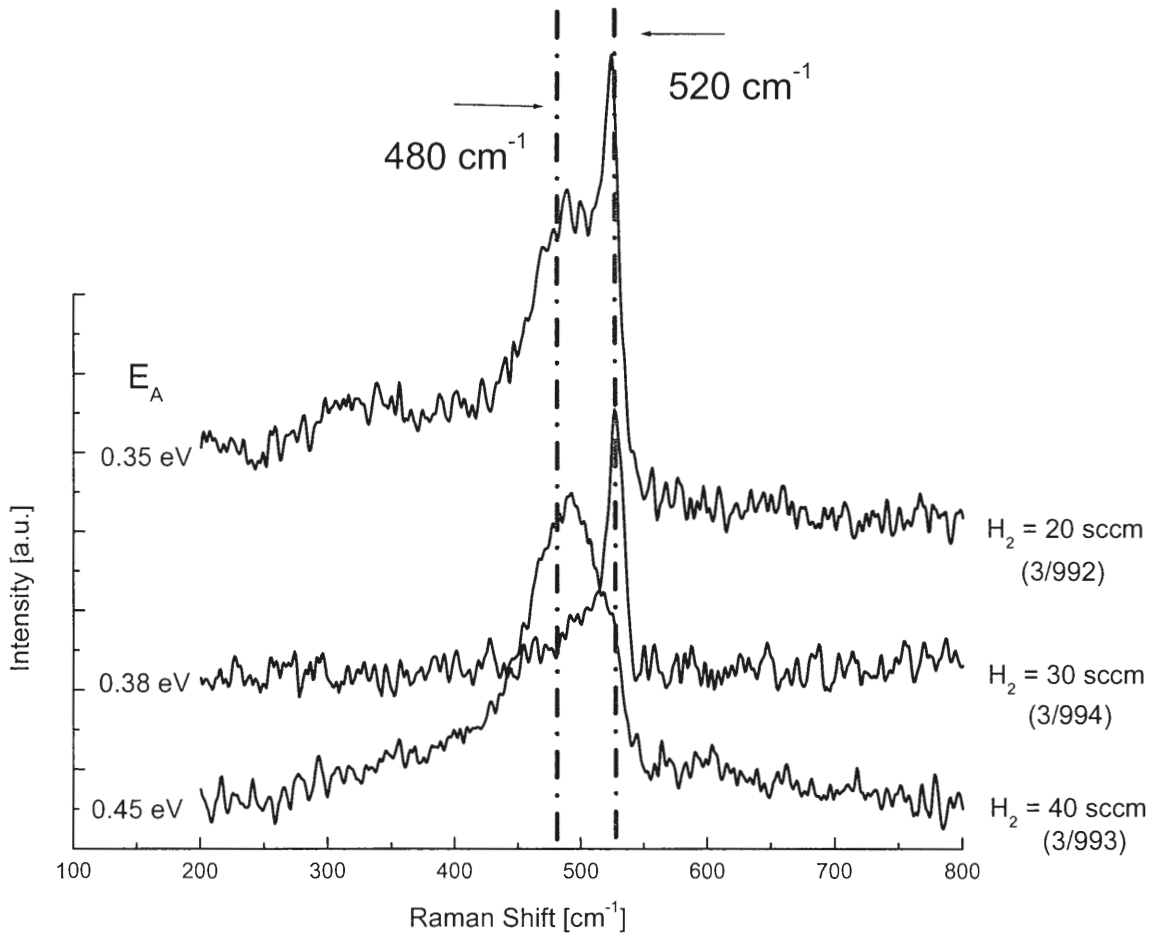


Figure 4.4. Raman spectra for He = 28 sccm.

Table 4.4. Properties of He = 0 sccm group.

Sample #	t [ $\mu\text{m}$ ]	rate [ $\text{\AA}/\text{sec}$ ]	Photosensitivity	$E_A$ [eV]	$\mu\text{c-} / \text{a-}$	$V_f$
980	1.17	3.2	$1.26 \times 10^0$	0.21	$\mu\text{c-Si:H}$	0.69
981	1.09	3.0	$1.18 \times 10^0$	0.23	$\mu\text{c-Si:H}$	0.74
982	1.02	2.8	$1.70 \times 10^0$	0.31	$\mu\text{c-Si:H}$	0.71
983	0.91	2.5	$1.46 \times 10^0$	0.53	$\mu\text{c-Si:H}$	0.72
984	1.36	3.8	$2.34 \times 10^0$	0.51	$\mu\text{c-Si:H}$	0.71

Table 4.5. Properties of He = 14 sccm group.

Sample #	t [ $\mu\text{m}$ ]	rate [ $\text{\AA}/\text{sec}$ ]	Photosensitivity	$E_A$ [eV]	$\mu\text{c-} / \text{a-}$	$V_f$
985	1.21	3.4	$2.28 \times 10^0$	0.28	$\mu\text{c-Si:H}$	0.58
986	1.06	2.9	$2.85 \times 10^0$	0.31	$\mu\text{c-Si:H}$	0.62
988	1.29	3.6	$2.07 \times 10^0$	0.40	$\mu\text{c-Si:H}$	0.69
989	1.22	3.4	$1.72 \times 10^1$	0.49	a-Si:H	0
990	1.01	2.8	$1.96 \times 10^2$	0.62	a-Si:H	0

Table 4.6. Properties of He = 28 sccm group.

Sample #	t [ $\mu\text{m}$ ]	rate [ $\text{\AA}/\text{sec}$ ]	Photosensitivity	$E_A$ [eV]	$\mu\text{c-} / \text{a-}$	$V_f$
992	1.22	3.4	$3.73 \times 10^0$	0.35	$\mu\text{c-Si:H}$	0.49
994	1.00	2.8	$6.91 \times 10^0$	0.38	$\mu\text{c-Si:H}$	0.83
993	1.25	3.5	$2.50 \times 10^0$	0.45	a-Si:H	0

Next, a set of six samples was prepared to study the substrate temperature effect. This samples were pre deposited with amorphous silicon layers for ten minutes in order to monitor the effect of having precursor of nucleation site. Ten minutes of amorphous layer was pre-deposited with 21 sccm of helium and 2.2 sccm silane and no hydrogen plasma gas under the pressure of 15 mTorr. For the purpose of comparison of the pre-amorphous layer deposition, a sample was prepared in the exactly same environment except this sample didn't have a pre-deposited amorphous layer. Sample #1050 is the one with pre-deposited amorphous layer and sample #1055 is the counter part. Surprisingly, there is no evidence observed in this experiment showing any improvement in the growth of microcrystalline layer with pre-deposited amorphous layer. No decisive conclusion could be drawn from this. Both turned out to have mixed phases and crystalline volume fraction is about 70 %. The other purpose of this set of experiment is to investigate the transition to microcrystalline phase as substrate temperature decreased down to 275 °C. The deposition parameter and properties of films are listed in Table 4.7 and 4.8, respectively. It was observed that as substrate temperature was set at 275 °C, there was no microcrystalline peak found. The Raman Shift spectra is plotted in Figure 4.5.

To confirm the presence of microcrystalline phase in films, x-ray diffraction (XRD) was measured. Figure 4.6 indicates prominent crystalline peaks at 28.1°, 47.2°, and 55.5° of  $2\theta$ , which correspond to (111), (220), and (311) planes. To extract background from 7059 glass substrate, XRD result from glass is plotted along with the film from each group. The average grain size in the microcrystalline films was determined by x-ray diffraction to be in the nanometer range. But due to the thin film thickness ( $\sim 1 \mu\text{m}$ ) comparing to the penetration depth of x-ray, grain size extraction is not meaningful with these samples.

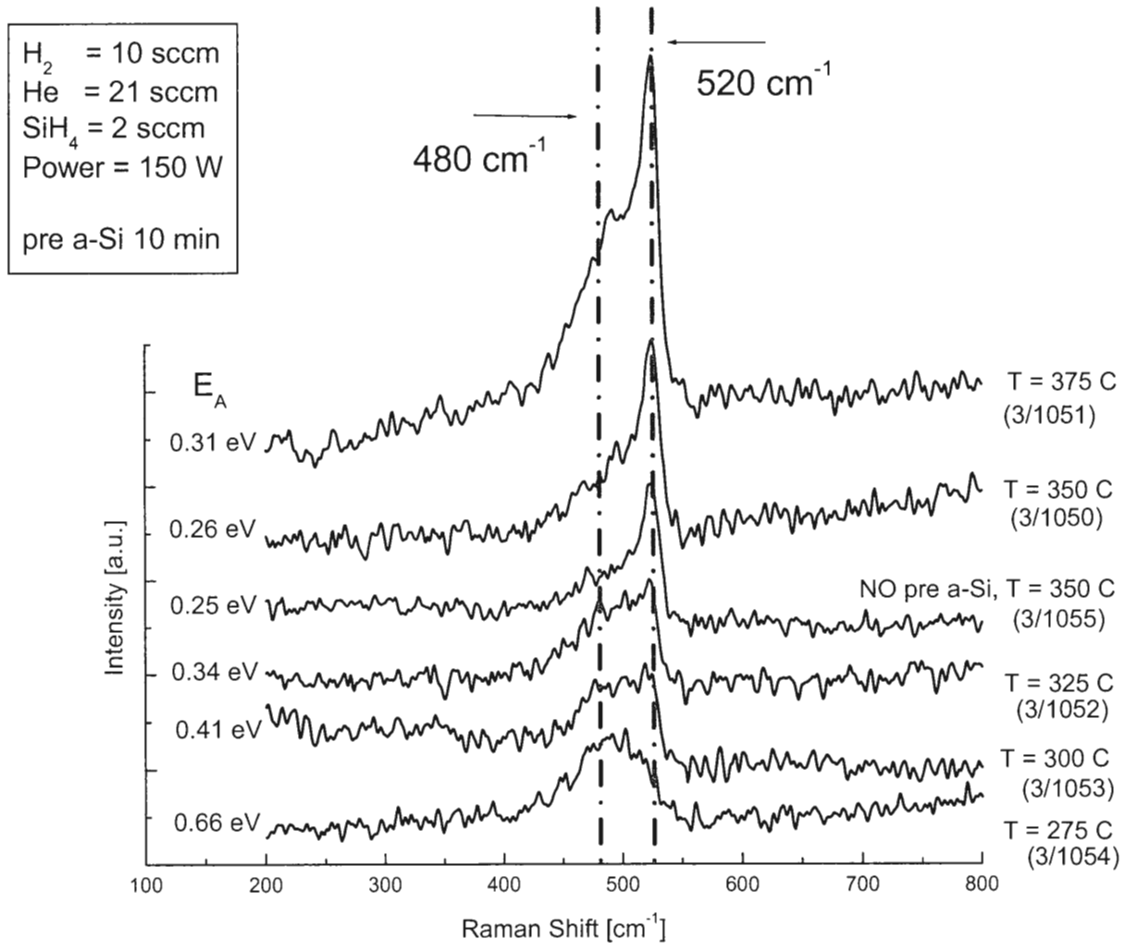


Figure 4.5 Raman spectra for decreasing substrate-temperature.

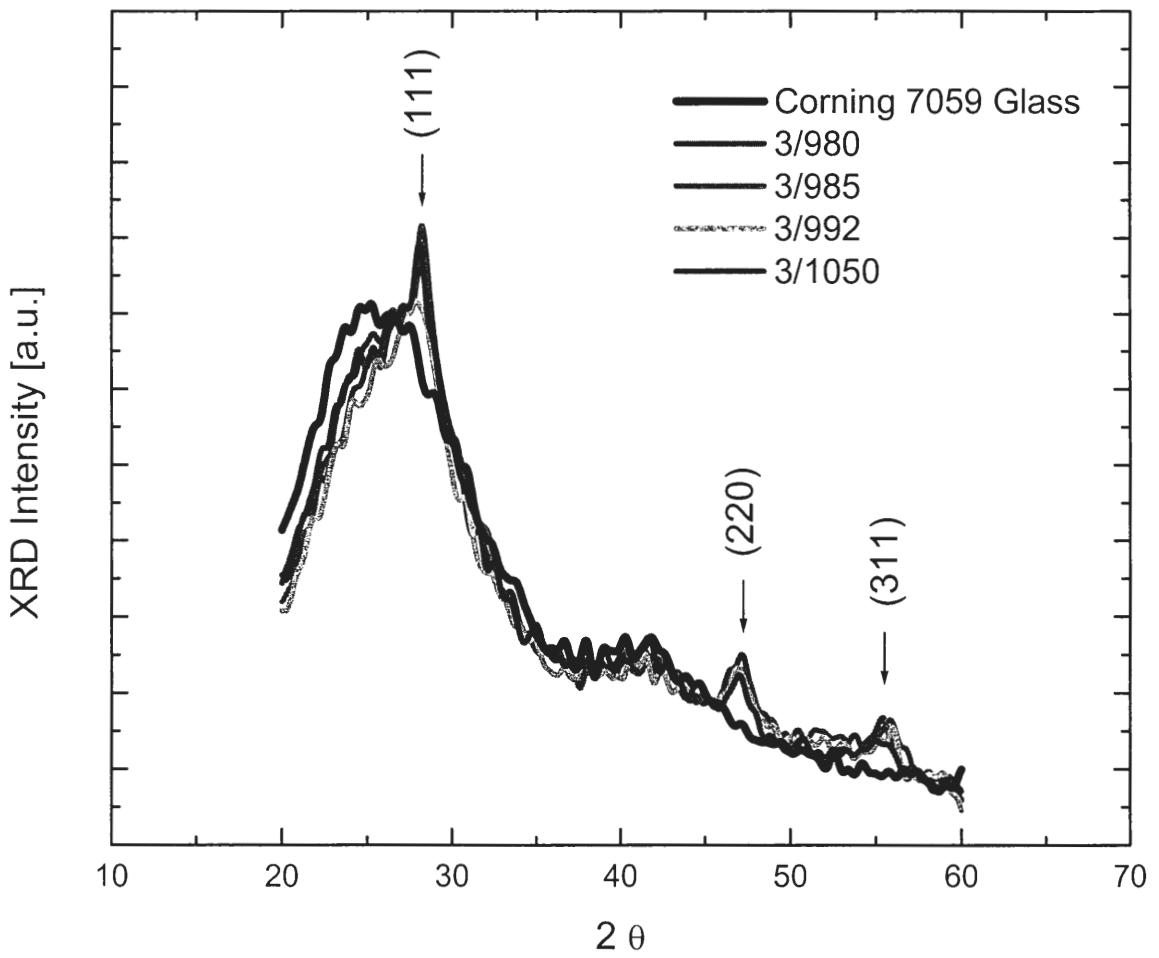


Figure 4.6 X-ray diffraction indicates prominent crystalline peaks.

Finally, hydrogenated microcrystalline silicon-germanium films [ $\mu\text{c}-(\text{Si}, \text{Ge})\text{:H}$ ] were deposited under the guideline of deposition of  $\mu\text{c}\text{-Si:H}$  films. The evidence of formation of microcrystalline phase came from the measurements of activation measurements and photosensitivity. The deposition parameters and material properties are listed in Table 4.7 and 4.8, respectively.

Table 4.7. Deposition parameters for [ $\mu\text{c}-(\text{Si}, \text{Ge})\text{:H}$ ] films.

Sample #	P	H <sub>2</sub>	He	SiH <sub>4</sub>	GeH <sub>4</sub>	H <sub>2</sub> /(SiH <sub>4</sub> +GeH <sub>4</sub> )
	[mTorr]	[sccm]	[sccm]	[sccm]	[sccm]	
1118	5	30	0	2	2	7.5
1122	10	40	0	2.3	2.3	8.7
1123	10	40	7	2.3	2.3	8.7
1125	10	20	7	2.3	2.3	4.4

Table 4.8. Properties of [ $\mu\text{c}-(\text{Si}, \text{Ge})\text{:H}$ ] films.

Sample #	t [ $\mu\text{m}$ ]	rate [ $\text{\AA}/\text{sec}$ ]	Photosensitivity	E <sub>A</sub> [eV]
1118	0.782	2.17	$1.19 \times 10^0$	0.23
1122	0.692	1.92	$1.11 \times 10^0$	0.18
1123	0.712	1.98	$1.13 \times 10^0$	0.19
1125	0.768	2.13	$1.15 \times 10^0$	0.20

## CHAPTER 5 CONCLUSIONS

Using a remote electron cyclotron resonance - plasma enhanced chemical vapor deposition (ECR-PECVD) process, thin films of hydrogenated microcrystalline silicon,  $\mu\text{c-Si:H}$ , and silicon-germanium,  $\mu\text{c-(Si,Ge):H}$ , have been deposited. The key variable in this work is the hydrogen dilution ratio to silane. It was found, through extensive film growth, that the low hydrogen dilution does lead to the deposition of microcrystalline silicon materials on foreign substrate at high growth rate with over 70% of crystalline volume fraction. High quality  $\mu\text{c-Si:H}$  thin film can be grown with dilution ratio of as low as 3.3. This is very contradictory to the previously accepted growth mechanism of microcrystalline phase, where it was regarded that the hydrogen dilution ratio should be more than 30 to grow microcrystalline phase. The addition of helium did not increase the growth rate significantly, but it quickly served as disrupting microcrystalline formation. This indicates the growth mechanism of microcrystalline phase is required to have quasi-equilibrium state during growth and it is quite different from that of amorphous phase. In addition, the substrate temperature-dependent phase transition was also observed. For ECR-PECVD system in MRC, the minimal substrate temperature is about 300 °C to grow microcrystalline materials with high microcrystalline volume fraction.

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