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Growth and characterization of microcrystalline silicon films and devices using very high frequency plasma enhanced chemical vapor deposition

by

Joshua Ali Graves

A thesis submitted to the graduate faculty in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Electrical Engineering

Program of Study Committee:
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This is to certify that the masters thesis of
Joshua Ali Graves
has met the thesis requirements of Iowa State University

Signatures have been redacted for privacy
To everyone who believes in me and who gave me the support to make it through this.
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ABSTRACT

This thesis is a report of the work done to grow hydrogenated microcrystalline Si materials and p-n junction photovoltaic devices using a 45MHz (VHF) PECVD process. Several parameters such as hydrogen dilution during growth, pressure, growth temperature, and ion bombardment were systematically varied during the growth process to study their effects on crystallinity and device properties. Crystallinity of the films was studied using Raman and x-ray diffraction techniques. It was found that the typical grain size was in the range of 10-25 nm, with larger grain sizes being obtained at higher deposition temperatures. It was also found that as the deposition pressure increased, the crystalline fraction decreased. This behavior is attributed to the decrease of ion bombardment at higher pressures. Optical measurements revealed the films to have absorption characteristics similar to those of c-Si. p+/n/n+ devices were fabricated on stainless steel and semi-transparent Mo/tin oxide substrates. Capacitance spectroscopy was used to estimate total defect and dopant densities in the base layer material. Good quality devices with fill factors approaching ~65% and open-circuit voltages of ~ 0.45 V could be fabricated using this technique. Diffusion length of holes in this material was estimated using quantum efficiency vs. voltage techniques, and it was found to be in the range of 1.2 micrometers.
CHAPTER 1: INTRODUCTION

1.1 Historical Perspective

Hydrogenated microcrystalline silicon (µc-Si:H) was fabricated for the first time in 1968 by Marecek and Veprek. They were first able to grow the microcrystalline silicon at a temperature of 600°C [1]. However in 1979, a doped microcrystalline silicon film was deposited with the use of hydrogen as an addition to the process gas [2]. A group from Japan was able to fabricate the film by using a high inductive silane glow discharge. Many studies and characteristics have been done on microcrystalline silicon films by PECVD (Plasma Enhanced Chemical Vapor Deposition) from then up to present [3].

Hydrogenated microcrystalline silicon along with amorphous silicon is an important material for solar cell fabrication. It is basically a small grained silicon material with grains in the range of 30 to 300Å. The grain boundaries are saturated with hydrogen or a thin layer of amorphous silicon tissues separating the grains. This presence leads to excellent minority carrier transport through the gains and minimizes recombination at the grain boundaries [10]. This has attracted many manufacturers because of the low costs. Early on, some researchers tried to make the entire solar cell devices out of microcrystalline silicon with little success. Microcrystalline silicon is a potentially good material for the intrinsic part of the solar cell, however it was not seriously considered to be of use for photovoltaic materials. The reason why microcrystalline silicon was not considered is because it was assumed to have a high defect density. This was believed to be because undoped µc-Si:H had strong n-type
characteristics, meaning high defect density. Later it was to be seen that oxygen contamination was mentioned as the explanation for the n-type characteristics.

A second reason why μc-Si:H was not taken seriously as a study for photovoltaic applications is the growth rate. Using standard PECVD application, the layers required for microcrystalline growth had long fabrication times. Typical depositions rates of microcrystalline silicon using PECVD were around 1 Å/s [4]. This means that it would take three hours of deposition time to grow a μc-Si:H film of 1μm in thickness.

1.2 Purpose of Research

Due to technologies and excellent optoelectronic properties that are obtained by improved deposition methods like VHF-GD (Very High Frequency – Glow Discharge), μc-Si:H is gaining interest in the scientific community. Many scientists are looking at μc-Si:H for use for thin film transistors. The VHF process has been shown to improve the deposition rate due to the increase in the dissociation of silane compared to the standard 13.56 MHz RF (radio frequency) PECVD [21]. A high density of H ions produced at lower energy removes excess H sufficiently. Due to the increasing frequencies, the maximum ion energies decrease with the frequency being below 130MHz [24]. However, too much energy causes damage to the lattice during growth. The growth process of PECVD films is a complex one which it still being disputed. A study of VHF PECVD parameters such as chamber pressure and silane flow, affect material properties and growth. The project objectives are:

- Use the existing RF PECVD reactor and modify/build it to deposit films using VHF PECVD.
- Use the new system to deposit μc-Si:H films and measure the properties of the
films.

• Determine the correlation of the crystal grain sizes with the change in temperature.

• Use the new system to deposit good quality $\mu$C-Si:H devices and measure the properties of the devices and material properties in devices.

I expect that new materials and devices at higher growth rates will be achieved through the experiments using VHF PECVD.
2.1 Growth Model

During the deposition, the growth chemistry is the determining factor for the electrical and optical properties of the film. The physics involved in the deposition process is highly complex and is mostly unknown due to the immaturity of technology. Some of the factors that affect growth chemistry are the many formations of the sub-species of radicals deposited on the substrate, chamber pressure, power, substrate temperature, and gas flow rates.

Two ways to promote microcrystalline film growth is to use low pressure and high power. Typical settings for the VHF PECVD system are a pressure of 50mT and a power setting of 40 – 45W. Doing a deposition at low pressures increases the ion bombardment and increases hydrogen (H) etching of the film. Homogenous films are grown when H ions are able to break the weaker bonds. As the power increases, the etching during growth by hydrogen also removes weak amorphous bonds, which leave behind the strong crystalline bonds[24]. However, etching during growth also reduces the growth rate. Due to the low pressure and high power technique, microcrystalline films can be grown at lower temperatures. Higher temperatures can be used to grow microcrystalline films; however at such temperature, hydrogen may evolve from the film, making it poorer quality.

When the plasma is ignited and the electrons collide with molecules, several different outcomes occur. Some of the possible outcomes are ionization, excitation, relaxation, dissociation, and recombination. Ionization process forms the plasma; excitation process is
where the gas species is raised to an excited energy state. The most important process for PECVD is dissociation. Recombination is the reversal of the dissociation process.

In plasma, dissociation of the gasses can lead to several chemical reactions. The silane (SiH₄) molecule can be broken down into SiH₃, SiH₂, SiH radicals. The growth of silicon films is believed to be dominated by the radical silyl (SiH₃), as in

\[ \text{SiH}_4 + e^- \rightarrow 2H + \text{SiH}_3. \]  

(2.1)

Figure 2-1: Possible Growth Conditions
In addition to this, one can also have

\[ \text{SiH}_4 + H \rightarrow \text{H}_2 + \text{SiH}_3 \]  

(2.2)

In figure 2-1, I show the possible pathways for film growth [4].

2.2 Plasma Fundamentals

The samples in this study were prepared using VHF PECVD. To understand the VHF process, some fundamentals of the plasma processing must be understood [5]. The field of plasma chemistry and plasma physics is too large of an in depth field to be analyzed at this time. The important concepts of plasmas for depositions will be discussed as an overview. For more detailed analysis of plasma physics see references [6, 7, 8].

To get a better understanding of the plasma physics it is helpful to look at a less technically inaccurate but conceptually helpful model of the deposition reactor.

Figure 2-2: Breakdown of Plasma
From the figure, it can be seen that an anode plate (positive charge) and cathode plate (negative charge) are enclosed by a volume of gas. There are a certain number of neutral species, ionized species, and free electrons in any given volume of gas enclosed. If a DC voltage were placed between the two plates, the free electrons will be accelerated toward the anode. Due to the small mass of the electron, the energy in the electric field will affect them the most. This is evident by comparing the thermal velocity of an electron to the velocity of an ion.

\[

v_{te} = \left( \frac{eT_e}{m_e} \right)^{\frac{1}{2}} \tag{2.3}
\]

\[

v_{ti} = \left( \frac{eT_i}{m_i} \right)^{\frac{1}{2}} \tag{2.4}
\]

where \( T \) is the temperature of the ion and electron, and \( m \) is the mass of the ion and electron. Since \( m_e / m_i << 1 \) and \( T_e > T_i \), the electrons are going to be the one that absorb most of the energy from the electric field.

As the free electrons are on their way to the anode, they will in turn hit the neutral species. Simple momentum transfer, excitation, ionization, and disassociation can result from the collision depending on the energy of the electron. An ion and two free electrons is the result of ionization interaction. These two new free electrons will also begin to accelerate toward the anode, causing more collisions. If the number of interactions are high enough most of the species in the volume will become ionized. When this process happens, it defines the gas as a plasma. However, once the electrons come into contact with the anode, the process ends and the plasma reverts back to a neutral gas.
If an insulating cathode with an AC applied voltage is used, the plasma can be maintained. The current will flow one way through the first half of the AC cycle. The ionization interaction will occur until the insulator is charged at which point the discharge will be terminated. During the second half of the AC cycle, the current will flow in the opposite direction through the plasma causing more ionization interactions. This goes on until the insulator is charged. If the cycle is fast enough, meaning the frequency is high, there is not sufficient time for the insulator to charge and a continuous breakdown is maintained. The frequency must be above 1MHz for this to occur. When the frequency is elevated in the range of 45MHz to 130MHz, the electrons will not accumulate on the anode and develop into an insulating layer. A major advantage of VHF process is that ion energy is lower than at 13.56MHz.

2.3 Reactor Description

The PECVD system was already set up and working before doing research. An RF function generator with frequency of 13.56MHz was finely tuned right when the plasma was ignited. However, a new system would have to be built to be able to increase the 13.56 MHz frequency to VHF or up to 45MHz in the Iowa State University deposition chamber.
A different function generator had to be used to achieve the VHF range. For the plasma excitation, a signal generator from 0.001 – 50MHz was used. To increase the power of the signal generator a broadband amplifier was used in a range from 1 to 100W. The amplifier was then connected to a variable inductance tuner, which is connected to the deposition chamber.

Optimum matching is achieved by minimizing the reflected power at a given frequency and then further adjusting the tuner to decrease the reflected power. However, a frequency must be chosen to be able to get optimum matching. Since the signal generator was limited to 50MHz, a decision to operate the signal generator at 45MHz was made.

It is critically important to have impedance matching for high frequency waves. High frequency waves behave much differently than low frequency waves. A combination of high quality, low impedance, and properly selected length of transmission line will provide the
best power transfer from the generator to the plasma chamber. The coaxial cable is the first section that power must be transferred through.

One reason the tuner was incorporated into the system was to have the ability to be flexible with the frequency and the cable length. The tuner is able to keep the reflected power down to 0.5W for the 45W forward power. With the presence of the tuner, it is also able to decrease the standing waves which can cause localized heating.

Figure 2-4: Reactor Setup
A schematic diagram of the deposition chamber system used for VHF PECVD is in figure 2-4. The power is introduced to the deposition chamber through the plate on top of the insulator. The gases are introduced in the deposition chamber through the bottom near the substrate parallel to the plate. This was simplified in figure 2-2 as early discussed. The plasma has to be tuned to acquire the lowest possible reflected waves and the specified forward power before depositing. The substrate holder is top loaded, which uses a stainless steel mask with a one-inch square to hold the substrate (glass, stainless steel) in place. The mask is bolted over the substrate to affix it firmly. The substrate holder also contains a heater block behind the substrate. This controls the temperature of the substrate.

The vacuum system contains a roughing pump and a turbo pump. The roughing pump reduces the pressure down from atmosphere to $\sim 10^{-3}$ Torr. The turbo pump is then activated and reduces the pressure from $10^{-3}$ to the range of $10^{-7} - 10^{-8}$ Torr. A backing pump, which is constantly purged with nitrogen, supports both pumps. This is to prevent build up of toxic gases used during the deposition process.

2.4 Substrate Cleaning

The 7059 Corning glass and the stainless steel substrates are cleaned in the same manner. Both glass and stainless steel substrates were cut to size and relatively clean when shipped by the manufacturer. All of the substrates are cleaned thoroughly before being loaded in the deposition chamber. The substrates are placed in a holder and boiled in acetone for 10 to 15 minutes to remove contaminants from the surface of the substrate. Next, the substrates are placed in methanol and put into an ultrasonic bath for 20 minutes to totally
2.5 Deposition Procedure

A standard operating procedure is strictly followed to maintain the film growth repeatability. Once the substrate has been cleaned and stored in methanol, it is taken out and blown dry with nitrogen before being placed in the substrate holder. The substrate holder is loaded into the VHF PECVD system and the system is purged with nitrogen to help remove any moisture inside the deposition chamber. While purging, the substrate is heated 50°C above the desired temperature of deposition. After the purges, the shutter is put in front of the substrate and a dummy layer is grown. The dummy layer places a fresh layer of silicon on the walls of the chamber to cover up any impurities while the shutter is closed to prevent depositing the impurities on the film.

During the actual deposition procedure, the temperature, hydrogen to silane ratios, forward power, and tuning are all adjusted. An amorphous layer is deposited on the glass first for 15-20 minutes. Then the microcrystalline layer is deposited. The length of deposition depends on the growth rate and desired thickness of the film. Deposition times range from 60 to 90 minute.

When the deposition is completed, the plasma is turned off and the film is cooled down to less than 150°C. While cooling down, the chamber is filled with $H_2$ and $SiH_4$ to a pressure up to 1 Torr to prevent oxidation. Now the film is ready to be characterized.
Optical measurements are performed before electrical measurements because metal contacts need to be evaporated on the film to do the electrical measurements.

![Figure 2-5: Device Structure](image)

Devices are also fabricated in the VHF PECVD, however the procedure is different. When the substrate is loaded, there is no depositing of a dummy layer. The substrate is polished stainless steel on which a 100nm $n^+$ a-Si:H is deposited. The $n^+$ layer is deposited to form a back contact. The gases are purged, and a dummy layer is deposited to remove memory of the $n^+$ layer. Next the undoped a-Si:H layer is deposited of 20-50nm. This layer seals up any shorts and significantly improves the device properties. Then the n microcrystalline Si:H base layer is deposited to a thickness of 0.8 to 2 micrometers thick. After that, a thin graded gap interfacial buffer layer is deposited to provide band gap matching between the n layer and the $p^+$ layer. The buffer layer also reduces electron
recombination at the interface. The final active layer is an $p^+$ a-(Si, C):H layer deposited at lower temperature (170°C) [10].

The first three layers can be deposited in the VHF PECVD system. Once the $n^+$ Si:H layer is done, the system needs to be purged to make sure all the phosphine is out of the manifold. Five purges of $SiH_4$ and $H_2$ along with 10 purges of $SiH_4, H_2$, and He are done to help remove the phosphine. Next, a dummy layer is deposited for 45 minutes to make sure the a-Si:H and microcrystalline will not be doped with the phosphorus. Once the three layers are done, the device is cooled and transferred to an ECR PECVD system to complete the buffer and $p^+$ layer. Transfer between the two systems must be limited to reduce the amount of airtime. Oxygen can dope the device if the device is in the air for a long period of time. When the $p^+$ layer is finished, the device is cooled and ready for ITO contacts for characterization.

2.6 Film and Device Contacts

Metallization

Electrical measurements for films are conducted by thermal evaporation of chromium contacts. The evaporation system consists of a diffusion pumped bell jar with resistively heated chromium rods. In figure 2-6, the mask on the left shows the mask that is placed in front of the film with an L/W ratio of 20. The film with the mask is loaded into the evaporator and pumped down to $3 \times 10^{-6}$ Torr to start the evaporation. The chromium layer is deposited at a rate of 5 Å/s to a thickness of 1000Å, which is measured inside the evaporator. After the film is taken out, silver paint is applied on top of the chromium
contacts to reduce contact resistance between the contacts and the metal probes. The films are annealed for 60 minutes at 200°C.

Figure 2-6: Chromium and ITO Contacts

ITO

Indium Tin Oxide (ITO) is used for contacts on devices for completing electrical measurements. In figure 2-6, the mask on the right shows the mask that is placed in front of the device when loaded into the deposition chamber. The chamber must be pumped down to $2 \times 10^{-6}$ Torr in order to start. Reactive RF sputtering in an Ar/O$_2$ plasma is used to deposit the contacts on the device. The pressure at deposition time is 5mT at a rate of 6-7 Å/s. The ITO contacts are deposited to a thickness of 2000Å with a 90% transparency. The device is taken out of the chamber and ready for measurements to be completed.
CHAPTER 3: CHARACTERIZATION TECHNIQUES

3.1 UV/VIS/NIR Spectroscopy

The spectrophotometer is used to determine the thicknesses of all films and devices fabricated. The apparatus used is the Perkin-Elmer dual beam spectrophotometer interfaced to a PC. This dual or split beam spectrophotometer generates a monochromatic beam, which is split by optics. The two beams are parallel to each other. One of the beams is used for a reference or directed at the photo-detector and the other beam is directed at the sample substrate for the interaction. The differences in the transmissions and reflections are then measured by the photo-detector.

For films, the beam is transmitted through the sample and the substrate. As it passes through both, some of the light is reflected by the substrate and some of the light is also reflected and absorbed by the sample. The interference with the light being reflected by the substrate and the light transmitted through the sample is the result of the interference pattern in figure 3-1.

The positions of the peaks or valleys in the interference are used to obtain the thickness of the film. The thickness of films and device can be calculated from the equation,

\[ t = \frac{\lambda_1 \lambda_2}{\beta n(\lambda_2 - \lambda_1)} \]  

(3.1)

where \( t \) is the calculated thickness of the film/device, \( n \) is the refractive index of film/device, \( \lambda_1 \) and \( \lambda_2 \) are consecutive peaks or a peak valley pair, \( \beta \) equal 4 for the peak to valley interval and 2 for peak to peak intervals.
3.2 Activation Energy

Activation energy is found by measuring the dark conductivity as a function of temperature of the film. This is a straightforward way to designate if the film is amorphous or crystalline. At the edge of a grain in the film, there exist surface states which are filled by elections. Band bending will occur since the electrons leave behind fixed donor atoms inside the grain. For an electron to transport from one grain to another grain, it must overcome the energy barrier between each grain. The only way to overcome the barrier is to tunnel through or jump the barrier thermionically. Tunneling is unlikely given the thickness of the barrier. Therefore, thermionic emission is a more likely mechanism for transport.
This technique requires the substrate to be placed on a heating block enclosed in a light tight box. This prevents light from getting in the box and causing excitation due to photon absorption. To enhance a current, a 100V bias is applied between the two probes on the film’s ohmic contacts. The heater block is then elevated in temperature up to 200°C.

The current is recorded in increments of 10°C until 100°C is reached. The activation energy is then calculated by the Arrhenius relationship

\[
I = I_0 e^{-\frac{E_A}{K_B T}}
\]

(3.2)

where I is the phonon current, \(I_0\) is the prefactor current, K is the Boltzmann constant, and T is the temperature. The Arrhenius plot is dependant on barrier height between grains. The activation energy is the slope of the linear line as seen in figure 3-3.
Low activation energy is an indication of the amount of crystallinity, and high activation energy indicates an amorphous film, since in amorphous silicon,

\[
\sigma = \sigma_0 \exp \frac{-(E_C - E_F)}{kT}
\]

(3.3)

and \( E_C - E_F \sim 1/2 \) (bandgap) \( \sim 0.8 \) eV [11].

### 3.3 Photosensitivity

Photosensitivity is the ratio of photo to dark conductivities, which give an indication of the crystallinity of the material since crystalline silicon is doped and have much higher dark conductivities than amorphous silicon. All samples are measured at room temperature in a light tight box with a fan on the sample to keep the temperature down. A 100V bias is applied between two probes on the film's ohmic contacts. A lamp is mounted directly above the sample that provides a one-sun light source. A shutter is also mounted between the sample and lamp to ensure the lamp has time to warm up for the illumination. The
photocurrent is measured when the shutter is opened and the sample is illuminated. Then the light is turned off and the box is closed up for thirty minutes to measure the dark-current. Closing the box for thirty minutes allows for any light induced carriers to recombine.

The currents are converted into photoconductivity and dark-conductivity by the expression

$$\sigma_{d, ph} = \frac{WL}{LVt}$$

where $W/L$ is the length to width ratio of the metal contacts which $\sim 20$, $I$ is the measured current, $V$ is the applied voltage, and $t$ is the thickness of the film. Conductivity is when free carriers in a semiconductor reach their thermal equilibrium given by

$$\sigma = qn_o \mu_n + qp_o \mu_p$$

where $n_o$ and $p_o$ are the electron and hole equilibrium concentrations and $\mu_n$ and $\mu_p$ are the electron and hole motilities. Amorphous materials generally have a dark-conductivity in the range of $10^{-9}$ to $10^{-11}$ while microcrystalline silicon materials have dark-conductivities in the $10^{-2}$ to $10^{-5}$ range. They both have approximately the same photo-conductivity.

3.4 Quantum Efficiency

Quantum efficiency is a measurement that can be used to accurately probe the absorption sub-gap states below $\alpha = 10^3 \text{cm}^{-1}$. This will give some insight on the quality of the films. The two-beam photoconductivity sub-band gap absorption technique was developed by Wronski and co-workers [12]. The UV/VIS/NIR spectrophotometer is limited to the thickness of the film, when taking measurements of absorption and reflection. The
films need to be at least 10µm thick to accurately determine $\alpha$, where $\alpha$’s are greater than $10^3 \text{cm}^{-1}$ from these measurements. Another benefit of using the two-beam sub gap technique is that it determines the absorption coefficients of films grown on non-transparent substrates such as stainless steel and polyimide.

When doing this measurement, the two-beam photoconductivity technique utilizes a DC light beam focused on the sample to fix the quasi-Fermi levels. The lifetimes of the photogenerated carriers will remain constant since the traps will be filled due to the continuous electron-hole pairs being created from the DC light.

While the DC light is on, an AC beam superimposes on the DC beam and modulates the additional created electron-hole pairs that can be detected by a lock-in amplifier. This makes it certain that the photocurrent due to the chopper frequency is detected. To obtain the signal a bias is applied across the sample to improve the transport of the electron-hole pairs. At each wavelength the absorption coefficient is calculated by dividing the measured signal by a reference signal and multiplying by the quantum efficiency of the reference detector.

By plotting $\alpha$ versus energy, the determination of the structure and quality of material can be found. The trend for crystalline silicon is a round absorption curve, where the trend for amorphous silicon is a curve that sharply drops to zero [13].
By comparing the two plots in figure 3-4, the left plot is a crystalline silicon type absorption curve. The more the curve of a film matches the curve of the crystalline silicon, the more likely the film will consist of microcrystalline structures. The round shape of the curve is a good electronic indication of the structure of the film.

Figure 3-4: Alpha versus Energy For Microcrystalline Silicon (left) and Amorphous Silicon (right)

Figure 3-5: Quantum Efficiency Setup
A schematic of the experimental apparatus is shown in figure 3-5. A monochromometer is used to change the incident photons wavelength of the white light. The usual wavelength is in the range of 400nm to 1300nm for silicon films. At the output of the monochromometer, a chopper is used to create the AC beam at a frequency of 13.5Hz. The frequency reduces the noise due to power lines at 60Hz and to ambient light.

When changing the wavelengths, high pass optical filters are needed at 700nm, 900nm, and 1200nm to reduce the second harmonics from the monochromometer. The filters also prevent photons of lower wavelengths from reaching the sample. The AC beam is collimated using two optical lenses and focused between the contacts on the film by a mirror. The absorption coefficient depends on the photon energy related to the band gap.

For devices, a difference in set up is needed. The AC beam is focused on the contacts and one probe is placed on the ITO contact while the other probed is placed on the stainless steel substrate. The wavelength from the monochromometer is recorded in the range of 400nm to 900nm. The measurement is taken at zero bias and at -0.5 bias for the given wavelength range. The quantum efficiency is then plotted by wavelength to see how efficient the cell is for the different wavelengths.

3.5 Raman Spectroscopy

Another nondestructive technique used to determine the degree of crystalline quality of thin films is Raman spectroscopy. The experimental system used is provided by the Material Science and Engineering department of ISU. The Raman effect occurs when incident photons are inelastically scattered by phonons, charge carriers, or impurities in the
material. Once an incident photon enters the material, it can either gain or lose energy. This is done by the creation or annihilation of a phonon in the material. This is called Stokes and anti-Stokes scattering.

Stokes scattering occurs when some of the stored energy is given to the crystal, which in turn creates phonons in the lattice. Anti-Stokes scattering occurs when the pre-existing phonons are annihilated by the stored energy. Since a phonon may either be created or destroyed, the equations follow the energy and momentum conservation rules:

\[ h \omega_s = h \omega_i \pm h \omega_p \]  
\[ hK_s = hK_i \pm hq_p \]

where the plus sign refers to the anti-Stokes scattering and the minus sign refers to the Stokes scattering. \( \omega \) refers to frequency, and \( K \) refers to the wave vector where the subscripts (s, i, p) refer to scattering, incident, and phonon.

Vibrational modes, in the material, result in the Raman spectra. However, the vibrational modes result in a polarized signal that is the longitudinal optic or the transverse optic axes for crystalline silicon [14]. Therefore, this simplifies the detection optics since the scattering is going to be limited to one vibrational mode at 520 \( cm^{-1} \). The vibrational mode at 520 \( cm^{-1} \) produces a sharp peak in the Raman spectra. As the momentum conservation of the scattering becomes more relaxed, a broad low intensity peak is a result. This low peak is a sign of the material becoming amorphous. An amorphous film produces a broad Raman peak at 480 \( cm^{-1} \). Figure 3-6 shows the Raman spectra with both amorphous and microcrystalline peaks for three films.
The frequency of the Raman bond, peak intensity, and peak width are three characteristics that provide information about the quality of crystalline in the film. Frequency is related to bond length, which, if shifted up, indicates compressive strains on the film. When the frequency is shifted down, the material becomes disordered. The peak intensity depends on the structural perfection of the film and is reduced in amorphous films. Peak width broadens as the material becomes disordered. This is caused by the relaxation of the momentum conservation in the scattering process. By measuring frequency, intensity, and Full Width Half Maximum (FWHM), a degree of crystallinity can be calculated by

\[
\chi_C = \frac{I_c}{I_c + mI_a} \quad [15] \tag{3.8}
\]
where $x_c$ is the percent of crystallinity, $I_c$ is the crystalline peak intensity at $520 \text{ cm}^{-1}$, $I_a$ is the amorphous peak intensity at $480 \text{ cm}^{-1}$, and $m$ is the ratio of cross section of crystalline phase to that of the amorphous phase. [14] This constant is equal to 0.88. [15, 2, 3]

The percent of crystallinity ($x_c$), can only be determined by deconvoluting the Raman spectra into two peaks. One part is the crystalline component and the other part is the amorphous component. The Origin program was used to deconvolute these two peaks to find the percent of crystallinity of the film. Figure 3-7 shows the microcrystalline peak after the Raman spectra had been deconvoluted.

![Graph showing Raman spectra](image)

Figure 3-7: Sample 4385

3.6 X-ray Diffraction

One way to characterize a film to determine the crystallinity or crystal structure of the film is to use x-ray diffraction technique. The x-ray diffractometer used to perform the experiments is maintained in the Material Analysis Research Laboratory of ISU. This measurement shows the peak position, peak height, peak width, and background which
corresponds to the phases present, phase concentration, crystal size, and amorphous content. The widths of the peaks indicate the average size of the crystal. If the width of the peak increases, it indicates that the size of the crystal has decreased. Peaks that are sharp have large crystals. In the x-ray diffraction, both the detector and x-ray source are swept through angles $2\theta$ as in the diagram.

![X-Ray Diffractometer Setup](image)

The application of Bragg’s Law is the principle of x-ray diffraction. The interference of reflected x-ray waves from a crystal is at a maximum when the angle of incident makes the path difference between the waves, an integer multiple of the wavelength [16]. The equation for Bragg’s Diffraction Law is

$$2d\sin\theta = n\lambda$$

(3.9)

where an x-ray beam of a wavelength ($\lambda$), strikes the planes in the crystal separated by a distance $d$ at an angle $\theta$, with $n$ being an integer. When the x-rays reflected distance differs from the planes by a complete number of $n$ wavelengths, diffraction occurs.
Microcrystalline silicon films will have diffracted peaks at values of 28.44°, 47.3°, 56.12°, and 69.12°. These different peak values correspond to different planes in the diamond cubic structure of the crystalline silicon. The corresponding planes are: <111>, <220>, <311>, and <400>. The two main planes, which show dominant peaks by the x-ray diffractometer, are the <111> and <220>. These two peaks and the <311> peak are shown in the following figure.

Figure 3-9: X-Ray Spectra Results

There may be a small peak at <311>, however <400> shows no peak at all. The reason for this is because the <311> and <400> plane peaks depend on the thickness of the films. To produce quality peaks at these planes, the film needs to be several micrometers thick to produce a signal. Since my samples are about one micrometer thick, the x-rays do not have the right amount of penetration depth to produce the <311> and <400> peaks.
3.7 Current-Voltage

The I-V measurement is another way of determining the electrical parameters of a solar cell. Solar cell parameters that can be found are open circuit voltage, fill factor, short circuit current and power. Open circuit voltage (Voc) is the voltage across the illuminated cell at zero current. The short circuit current (Isc), is the current through the illuminated cell if the voltage across the cell is zero. The maximum power is obtained at a voltage labeled as $V_m$ with $I_m$ being the current at that voltage. The fill factor (efficiency of the solar cell) is defined as the ratio of the maximum power of the cell to the product of the Voc and Isc or

$$FF = \frac{I_m V_m}{IscVoc}.$$  \hspace{1cm} (3.10)

In this technique, the probes are placed on the ITO contacts of the sample and the stainless steel substrate. A lamp is mounted directly above the sample that provides a one sun light source. There is also a shutter between the lamp and sample to allow the lamp enough time to heat up. The shutter is moved and a voltage from 1V to -1V is applied. A program plots the I-V curves and determines the electrical parameters of the device. After the measurements are taken, the sample is put into the oven at 200°C for 15 to 20 minutes for the ITO contacts to anneal and punch through any thin oxide layer. Then the measurement is taken again to determine if the quality of the solar cell improved.

3.8 Capacitance-Voltage

Capacitance-voltage can determine the substrate doping and built-in voltage of a semiconductor device. Within a semi-conducting device, the capacitance-voltage measurement determines the movement of charge. When a reverse DC bias is applied to the
sample the depletion width is changed and the majority carrier concentration is obtained as a function of depth. If

$$\partial Q = qAN_D(x)dx$$

(3.11)

and

$$C = \frac{\partial Q}{\partial x} \cdot \frac{\partial x}{\partial V}$$

(3.12)

where \(\frac{\partial V}{\partial x} = \frac{q}{\varepsilon} N_D(x) \bullet x_D\), then the capacitance can be expressed as

$$\frac{A^2}{C^2} = \frac{2\varepsilon}{qN_D(x)V}$$

(3.13)

where \(N_D(x)\) is the doping, \(A\) is the area, \(\varepsilon\) is the permittivity of silicon, and \(V\) is the applied voltage.

At room temperature, probes are placed on the device ITO contacts and a reverse bias is applied. The voltage is raised in increments of 0.1 V from 0 V to 3 V. A box is placed over the device to reduce any interference by light. From the variation in the voltage a capacitance can be obtained at each incremented step. By plotting \(\frac{1}{C^2}\) versus \(V\), one obtains a slope proportional to the carrier concentration as a function of depth. Please note that for materials with deep defects, this measurement gives only an approximate magnitude of donor density. By extrapolating the slope so it intersects the x-axis, the built-in voltage can be obtained as figure 3-10 shows.
Figure 3-10: Capacitance-Voltage Graph to Obtain Doping Concentration
CHAPTER 4: RESULTS

Microcrystalline silicon films had been deposited in the RF PECVD before this study and several depositions were executed using RF of 13.56 MHz to determine baseline parameters for the microcrystalline silicon using VHF. When the first depositions began, microcrystalline silicon was deposited directly on 7059 glass. However, all films with the first layer deposited using microcrystalline parameters did not have the characteristics of hydrogenated microcrystalline silicon. In other studies, an amorphous layer was deposited before the microcrystalline layer. It was found that the presence of an underlying amorphous layer facilitated the growth of microcrystalline silicon. The a-Si:H layer provides good nucleation sites as compared to glass. When using stainless steel substrates to deposit microcrystalline silicon, metal induced crystallization phenomena provide nucleation sites so an amorphous layer is not always needed to start the deposition, though this phenomena is not stated in detail.

In the VHF process, the amorphous layer was deposited at 10W at a low hydrogen dilution (5:1) and the microcrystalline silicon at 40W. The hydrogen dilution for microcrystalline silicon was (12:1). Calibration funs were performed to measure growth rates. Learning how to run the reactor using RF PECVD gave a basis for how long it takes to deposit a film of one micrometer. From start to finish with: purging, pumping down, heating up, depositing the film, and cooling down the system it takes 3.5 to 4.5 hours for each deposition. The deposition runs and characterizations are tabulated. The table shows
depositions at different temperatures, pressures, and hydrogen dilution ratios which were used.

Table 4-1: Film Depositions

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<thead>
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<th>sample #</th>
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<th>press (mT)</th>
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<th>Vrf</th>
<th>Vdc</th>
<th>H2</th>
<th>SH4</th>
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<th>t (um)</th>
<th>(I/photo)</th>
<th>(I/dark)</th>
<th>AE(eV)</th>
<th>type of layer</th>
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<th>Growth rate (A/s)</th>
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One of the first characterizations of all the films is the activation energy. In general, lower activation energy (0.1-0.3eV) indicates microcrystalline silicon while higher activation energy (0.7-0.9eV) gives the indication of amorphous silicon. In figure 4.1, the activation energy of many samples is plotted as a function of hydrogen dilution at various pressures.
Films that are deposited at lower pressure increases ion bombardment and the probability that microcrystalline silicon is going to form. With less pressure in the reactor, hydrogen ions and silyl radicals will be able to travel further and more will be able to make contact (break weak bonds) with the substrate to deposit. At deposition pressures of 50mT and 100mT, the film favors microcrystalline silicon throughout the different $\frac{H_2}{SiH_4}$ ratios.

![Activation Energy vs H2:SiH4](image)

Figure 4-1: Activation Energy vs. Hydrogen Dilution Ratio

As stated before, the greater the hydrogen dilution, the more collisions and interactions there will be when more H ions are added, the weak Si-H bonds break and leave the strong Si-Si bonds in the growing film, which is necessary for the growth of microcrystalline silicon films. The data for the deposition pressure of 200mT in figure 4-1 shows this phenomenon clearly. With a low hydrogen dilution ratio, the film appears to be
more amorphous, as indicated by activation energy. However, as the hydrogen dilution ratio
increases, the activation energy starts to drop and the crystallinity of the film becomes better.

The deposition at the pressure of 500mT is different from all other pressures because
as the pressure in the chamber increases the crystallinity of the film decreases. The 500mT
films start out as poor amorphous films yet as the hydrogen dilution is increased the films
show better amorphous silicon characteristics. At high hydrogen dilution, high pressure
depositions, there is more $H_2$ in the plasma, however due to the high pressure in the
chamber, ion bombardment is not adequate and film does not become microcrystalline.

As stated earlier in the paper, the growth rate of microcrystalline silicon using VHF
started at 1Å/s. There have been reports of microcrystalline silicon growth using VHF from
6 to 10Å/s and the most recent studies with 6 to 10Å/s have good quality microcrystalline
films [17]. Some other studies have reported a 20+Å/s growth; however the quality of the
microcrystalline silicon film was not good due to $H_2$ being trapped in the lattice [18]. The
growth rate in our VHF PECVD system has almost reached 5Å/s. From the figure below, the
growth rate can clearly be seen for the different pressures and hydrogen dilution ratios.

As $H_2$ dilution is increased, the growth rate of microcrystalline silicon at every
pressure decreases, which is expected due to the etching effect of the H ions. Adding $H_2$ is
good for the crystallinity of the films but bad for the growth rate because as $H_2$ is added to
the plasma, H ions break the weak Si-H bonds leaving the strong Si-Si bonds. This etching
away of the film reduces the growth rate. Maintaining a high growth rate of microcrystalline
silicon is strongly dependant on the etching of $H_2$ and $H_2$ dilution.
The ratio of photo to dark conductivity is known as photosensitivity and discussed earlier. The figure below shows the relationship between photosensitivity and hydrogen dilution. As in the activation energy plot in figure 4-1, the chamber pressures of 50mT and 100mT have a photosensitivity of almost one, which is a good indication of microcrystalline silicon.
The chamber pressure of 200mT demonstrates how the ratio of $H_2$ to $SiH_4$ affects the crystalline growth of the film. As more $H_2$ is added to the plasma, the film is no longer in the amorphous region, it becomes more crystalline and quality improves. As seen in the activation energy plot, the 500mT films remain amorphous as indicated by photosensitivity. At this pressure photosensitivity does not decrease down into the region of microcrystalline silicon signature and therefore, 500mT is not a good pressure to deposit microcrystalline silicon in our reactor geometry and at our power levels.

Typical microcrystalline silicon films are composed of small crystals with an average grain size of 30 to 300 Å that are embedded in an amorphous layer. The sizes of the grains in silicon depend on pressure, $H_2$ dilution ratio, and the temperature of the substrate. In general, the larger the grain sizes of the film, the better one expects mobility to be, and hence better photovoltaic properties. Microcrystalline silicon is also important for thin film transistors, because the electronic properties get better with the larger size of the grain [18, 19].

A useful method of determining the grain size of a film is using x-ray diffraction, which was discussed earlier. By measuring the broadening of the peaks using the Debye-Scherrer equation of the x-ray spectra,

$$\frac{.9\lambda}{B \cos \theta}$$

(4.1)

the crystallite grain size can be found because as grain size decreases, the x-ray diffraction spectra shows a wider peak. With the use of x-ray diffraction, grain size is plotted versus the $H_2$ dilution ratio in the figure below.
Since the electronic measurements did not indicate microcrystalline silicon for 200mT and 500mT pressures, these pressures were not included in the graph. The x-ray diffraction was taken at these pressures, however no peaks were found at the $<111>$ and $<200>$ planes, which are the typical morphology seen in microcrystalline silicon.

Figure 4-5: Temperature vs. Grain Size
As hydrogen dilution was increased, the grain size increased. This phenomenon was expected since H ions break weak Si-H bonds and etch away the amorphous silicon, leaving only strong Si-Si bonds leading to the growth of crystals in the film. Temperature plays a role in increasing the size of the grains also. As temperature increases, it is easier for the bonds to be broken because of the lattice vibrations and mobility, so the higher the temperature, the larger the grain size should be. The figure above demonstrates this fact as the indicated temperature was varied from 350 to 500°C for the same hydrogen dilution. Note that the temperature in the figure is the indicated temperature. The real temperature may be ~50-70°C lower [23]. Since the limit of the substrate heater is 500 to 550°C, no films were deposited at temperatures higher than 500°C.

A good way to test the electronic quality of a material is to make photovoltaic devices using microcrystalline silicon. With a device, one wants to reduce the thickness of the film to what is actually needed to absorb most of solar radiation, and the reduction in process temperature will enable the use of low-cost substrate materials making device fabrication cost effective. Also, the use of a process where large area fabrication and integration into modules is why microcrystalline silicon is considered for photovoltaics. As shown in figure 2-6, the microcrystalline silicon is base the n-layer and the thickest layer of the solar cell.

A number of $p^+nn^+$ devices were fabricated to study the relationship between process parameters and device and material properties. The better microcrystalline silicon films grown with VHF were used as the n-layer for the fabrication of the device. As seen in the Table 4-2 below, the devices consisted of a back $n^+$ layer followed by a thin a-Si:H layer to seal up any shorts, which was then followed by the n microcrystalline base layer, followed by
the top $p^+$ layer. In some of the devices, the microcrystalline n layer was graded in $SiH_4 : H_2$ ratios. Just prior to the p layer, there was always a graded composition layer, whose purpose was to increase the amorphous fraction. Thereby increasing effective bandgap and driving electrons away from the interface with the p layer.

Table 4-2: Device Depositions

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<th>reflect</th>
<th>Vbf</th>
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<th>He</th>
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Figure 4-6: Sample 4420 I-V Curve
With this experiment the current-voltage curves of 3 devices are shown. Figure 4-6 shows the characterizations of a device with a non-changing n-layer. The device is deposited with a $H_2/\text{SiH}_4$ ratio of 60/4 sccm. The corresponding film deposited with the same parameters had low activation energy and great crystallinity characteristics. This device was deposited at 350°C for the n-layer and had a Voc of 0.424V. The fill factor for this microcrystalline cell is 0.515, which is not very good. Other studies have recorded fill factors of up to 0.7 for devices [10]. This device is a solar cell that has potential for improvement. Other devices deposited with non-changing n-layer produced similar results.

In figure 4-7, two similar depositions are shown. Both depositions are prepared the same except 4449 starts the first 10 minutes of the microcrystalline silicon layer at a hydrogen dilution ratio of 20:1, where 4450 starts at 15:1. Both have the first layer beginning at 400°C to form the larger grains and then cooled to 350°C for the rest of the deposition. The two films have been improved since changing the hydrogen dilution ratio of the n-layer. However, 4450 is the better of the two devices.

![Figure 4-7: I-V Curves for Samples 4449 and 4450](image)
The two devices have a similar Voc of 0.45V except 4450 has a slightly greater Voc by 0.01V. The fill factor of 4450 is also slightly greater than that of 4449. The fill factor is 0.659 where the fill factor of the other device is 0.648. This means that the device is more efficient than the other two devices shown. Sample 4449 has a higher quantum efficiency of 0.074 at 800nm than the other devices, which indicates it more effectively harnesses the solar energy by being able to absorb radiation at higher wavelengths.

![Figure 4-8: Quantum Efficiency for 4450](image)

Microcrystalline silicon makes use of the sun's spectrum of near infrared. Amorphous silicon absorption for short wavelengths is much stronger than microcrystalline silicon. However, amorphous silicon devices do not surpass 800nm in quantum efficiency. Microcrystalline silicon is able to absorb radiation and collect carriers of 800nm and higher.
which has the potential to absorb more of the solar spectrum and be more efficient than amorphous silicon devices.

Using the capacitance-voltage measurement as discussed earlier can give an indication of the defect density of the base n-layers for the devices. The defect density levels for 4449 and 4450 were both in the range of $3 - 5 \times 10^{17} \text{ cm}^{-3}$. These are very high (defect and doping) densities and will need to be reduced if better devices are to be obtained.

To achieve lower (doping and defect) densities, we used lower substrate temperature and also compensated the material by using ppm levels of trimethylboron (TMB). The results of such comparisons are shown in figure 4-10, where we plot effective defect density versus TMB flow. Quite clearly, increasing TMB flow significantly reduces defect density by $\sim 2$ orders of magnitude.
Diffusion length of holes (L), was measured using capacitance and relative quantum efficiency at long wavelengths (860-900nm) under varying reverse bias. By changing the bias, we change depletion width. For photons whose $\alpha$ is small ($\alpha L \ll 1$, $\alpha W \ll 1$, $\alpha t \ll 1$) and films such that $L \ll t$, it is easy to show that

$$QE \sim \alpha(W_0 + L)$$

(4.2)

where $W_0$ is the depletion width and $L$ is the diffusion length. ($t$ is the thickness of the base layer). In figure 4-11, we show the relative quantum efficiency for device 2/6403.
Figure 4-11: Relative QE vs. Voltage With No TMB

The points are experimental data and the line is a fit to equation 4.2, with the value of L (the only unknown parameter) as 0.2µm.

In figure 4-12, we show how L changes as a function of TMB compensation. We find that as the quality of films becomes better with the incorporation of TMB, the diffusion length of holes increases, reaching 1.2µm, in the same range as for other good quality VHF microcrystalline silicon.
Having the largest crystals size does not guarantee the device is going to be a good solar cell. In order to obtain a good solar cell, the grain boundaries must be passivated. Without having the grain boundaries passivated, the recombination centers increases, which destroy the mobility in the solar cell. Due to the higher temperatures of the chamber for sample 4450, passivation of the grain boundaries may have decreased. The increased surface mobility and lattice vibrations from the increased temperature will prevent the weak hydrogen bonds to form. To test this, sample 4487 was deposited with the exact same parameters as sample 4450. However, after the amorphous layer was deposited, the microcrystalline layers’ temperature was decreased to 250°C instead of 350°C. For sample 4487, the fill factor jumped up to 0.674 and the Voc to 0.52V. This device has been the best
solar cell deposited by VHF here thus far. This proves that passivation of the grain boundaries for the microcrystalline silicon with hydrogen is crucial to decrease the recombination in the solar cell.
CHAPTER 5: CONCLUSIONS

5.1 Conclusions

There are a number of results that were obtained through this study. First a new deposition system, VHF-PECVD was built and made operational to grow both amorphous and microcrystalline Si films and devices. Microcrystalline Si:H films were grown under deliberately varied process conditions to establish the relationship between film properties and processing conditions. It was found that pressure and hydrogen dilutions were major variable in growing good quality microcrystalline Si:H films. Lower pressures led to a higher degree of microcrystallinity even at low hydrogen dilution ratios (12:1). At high pressures (500mT), the films were never microcrystalline even with high hydrogen dilution ratios (30:1). In general, except for the highest pressures, hydrogen dilution increased the microcrystalline fraction in the film.

A set of characterization tools, including activation energy, Raman spectroscopy, and x-ray diffraction were used to characterize the films. It was found that there was a very good correlation between activation energy and degree of microcrystallinity. A low activation energy (~0.1-0.2 eV) almost always meant a high degree of microcrystallinity. In contrast, films which were amorphous tended to have a much higher activation energy (~0.5-0.7 eV). It was found that growth temperature had a profound influence on the grain size of the microcrystalline layer. The grain sizes changed from ~10 nm to ~25 nm as the temperature increased from ~250 C to 450 C.
Proof-of-concept p+nn+ devices were made in these films. The devices showed good fill factors and voltages, and a QE that extended to 800 nm, indicating that the n (base layer) materials were microcrystalline in the device. The devices were used to measure the total (doping + defect) densities in the material, using low-frequency capacitance techniques. It was found that the total density decreased significantly as compensating agent B was added to the gas mixture. This fact indicates that much of the defect is due to either the memory of the previous n+ layer being left on the reactor walls, and thereby contaminating the base n layer, or oxygen dopant coming from outgassing from the walls of the reactor. B will compensate either P or O, and reduce the (doping + defect) densities. Without compensation, the densities were in the range of a few $10^{17}$/cm$^3$, but with added compensation, they reduced to a few $10^{15}$/cm$^3$ in range.

Diffusion length of holes was measured using a reverse bias quantum efficiency technique. It was found that if no compensation was used, the diffusion lengths were very small (~0.2 micrometer). But, as the degree of compensation increased, the diffusion length increased to 1.2 micrometer, in the same range as the best materials reported in the literature. Reasonable growth rates, in the range of 5 Å/sec were obtained. Devices were made at these growth rates.

5.2 Future Work

Many settings can be altered to study the crystallinity of the microcrystalline silicon using VHF PECVD. Since our apparatus was limited to 45W incident, higher wattage can be explored to see if there is an effect of the crystallinity of the silicon. Comparing the
microcrystalline silicon in a range from 30W to 80W would be interesting. Higher frequencies could be introduced to the plasma to compare with the 45MHz used in this study. The signal generator is limited to 50MHz. Being able to increase the frequency from 40 to 120MHz would be a good way to study the effects on the crystallinity of silicon. All films and devices were deposited on 7059 glass and stainless steel substrates. Determining a process to deposit microcrystalline silicon on polyimide, which would have to take into account temperature, is another step that can be taken. To be able to deposit microcrystalline silicon at low temperatures would advance the microcrystalline silicon in industry due to the costs and the ability to use different substrates.

A big step to fabricating devices is having one deposition chamber doing the whole process. Switching back and forth from one deposition chamber to another ensures the device to being exposed to oxygen in the airtime. Having a single chamber system is a major disadvantage in that cross-contamination of the base layer from a previous doped layer is very likely. A multi-chamber should be built. Lastly, a study that should be attempted is fabricating thin film transistors with microcrystalline silicon using the VHF PECVD process.
REFERENCES


[23] V. Dalal, “Fundamental Considerations Regarding the Growth of Amorphous and Microcrystalline

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