Characterization of polycrystalline silicon films grown by LPCVD of silane

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Characterization of polycrystalline silicon films
grown by LPCVD of silane

by

Justin Bradley Dorhout

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:
Gary Tuttle (Major Professor)
Vikram Dalal
Rana Biswas

Iowa State University
Ames, Iowa
2006
This is to certify that the master’s thesis of

Justin Bradley Dorhout

has met the thesis requirements of Iowa State University

Signatures have been redacted for privacy
To my parents,

with love and gratitude.
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Abstract

Deposition of polycrystalline silicon by thermolysis of silane, SiH₄, is a common technique for creating polysilicon films for a variety of applications. The deposition temperature and pressure greatly influence parameters relating to growth rate and film quality. These characteristics include film crystallinity and resulting grain orientation that determine the optical and electrical properties of the films and their suitability for particular applications. An empirical approach was taken to characterize the growth process and resulting film quality. Polycrystalline silicon films were grown to map a region of temperatures and pressures in the range of 575°C to 700°C and 200 mTorr to 500 mTorr. Deposition rate increased with increasing pressure, and was a strong function of temperature, increasing quickly then diminishing due to silane depletion. The crystallinity of films increased with temperature and decreased with pressure, exhibiting regions of rapid transition between amorphous and crystalline phases. X-ray diffraction was used to determine grain orientation and size. The <220> grains showed preferential growth while <111> and <311> grains were completely inhibited at low temperatures. Band gap energy decreased with increasing temperature and crystallinity. Resistivity of as-deposited, intrinsic films was very high. However, planar source phosphorus diffusion and annealing reduced resistivity to as low as $2.5 \times 10^{-3} \, \Omega \cdot \text{cm}$. 
Chapter 1: Introduction

1.1 Historical Perspective

For several decades, thermolysis of silane through low-pressure chemical vapor deposition (LPCVD) has been utilized in the fabrication of MOSFET gate electrodes as well as load resistors in integrated circuits [1]. Polycrystalline silicon (polysilicon) has also demonstrated properties desirable in the making of EEPROM memories and thin-film transistors [2], most often arrayed to drive display elements. Moreover, polysilicon films produced by means of low-pressure chemical vapor deposition were applied toward the fabrication of thin film solar cells although innovation of alternate techniques such as plasma-enhanced CVD and hot-wire CVD have diminished the market share of polysilicon due to the thermal economy of these techniques [3].

Polysilicon has now been used extensively in the nascent field of micro- and nano-electromechanical devices; certainly in part owing to the vast body of work and knowledge developed for microelectronic research and the existing infrastructure.

1.2 Motivation and Objective

Given the volume of research available describing the many properties of polysilicon, this work was undertaken to characterize and understand a particular LPCVD system to the end that polycrystalline silicon films may be deposited with relative control over film properties such as thickness, resistivity, crystalline volume, grain orientation, and optical behavior[4]. While physical constants relating to the use of silane in LPCVD applications are known in detail, the behavior of a particular LPCVD system is a mixture of a number of variables. These variables include effects such as substrate temperature gradients and gas-
source depletion [5]. Therefore, while previous research is invaluable in learning the principles of LPCVD and regime of operation, an empirical approach best suits the optimization of a particular system. This work is largely motivated toward produce a tool for use in the synthesis of future research.
Chapter 2: Fundamentals of Low-Pressure Chemical Vapor Deposition

2.1 Chemical Source

Polycrystalline silicon (polysilicon) is generally deposited by chemical vapor deposition utilizing thermolysis of silane, SiH₄. Silane may be reacted to form silicon films over a great range of pressure and temperatures, including atmospheric pressure if in the presence of a carrier gas (H₂, N₂, He), to the exclusion of oxygen [5].

2.2 Reactor Type

The deposition system utilized in these growths is a “hot-wall” low-pressure chemical vapor system operating on the principle of heating pure silane to high temperatures at pressures on the order of a few hundred mTorr. Low pressure benefits the deposition in two ways. First, the vacuum created in the chamber limits the presence of oxygen. Silane is pyrophoric and combusts in the presence of oxygen at room temperature. Additionally, it is desirable to limit the amount of oxygen in the reactor as SiO₂ will be incorporated into the film and lower the quality and crystallinity [6].

The second advantage of operating a reactor in a low-pressure regime are the kinetics of the decomposition and deposition of silane. At lower pressures, the mean free path of silane molecules is increased. The molecule will undergo fewer collisions so that gas-phase reactions are reduced. Moreover, as the reactive species diffuse through the boundary layer and absorb onto the substrate surface, they will diffuse until they desorb or incorporate into a low energy bonding arrangement. The longer the diffusion length of the species, the more ordered the film will become. However, should two or more diffusing species with relatively
low kinetic energy collide and bond, they could begin the nucleation of another grain and lower the crystallinity of the film. Therefore, lowering the population of diffusing species on the surface of the film will increase the crystallinity of the deposited film. The surface species population is determined by the rate of arrival, which is related to the partial pressure [7]. Hence, lower chamber pressure translates into higher crystallinity at a given temperature.

2.3 Reaction Chemistry and Kinetics

Very simply, one mole SiH₄ decomposes into one mole Si and two moles H₂.

$$SiH_4 \rightarrow Si + 2H_2$$  \hspace{1cm} (2.1)

The kinetics of the reaction are considerably more complicated however, and a full treatment will not be provided here [8]. It is thought that silane-based reactions are dominated at the surface by silane and silylene (SiH₂), and less often by silyl (SiH₃).

The reaction rate is usually limited by one of two factors: the arrival rate of reactive species or the rate at which the reaction will occur at a given temperature. These are typically referred to as mass-transport limited reaction and surface-rate limited reactions. The surface-reaction rate is a strong function of temperature, and follows an Arrhenius relation which increases exponentially with temperature [5].

$$surface\ rate \ \propto \ \exp\left(-\frac{E_a}{kT}\right)$$  \hspace{1cm} (2.2)

For silane, $E_a$ is reported between 1.6 eV – 2.0 eV. A small deviation in temperature results in a sizable change in reaction rate. The mass-transport rate has a slight positive
correlation with temperature but is mostly determined by the partial pressure of silane at the reaction location and will generally increase linearly with pressure. At higher temperatures LPCVD reactors operate exclusively in mass-transport rate limited regime, at lower temperatures operation is confined to the surface-rate limited regime. This effect is illustrated in Fig. 2.1.

![Figure 2.1 Temperature dependence of silicon epitaxial growth for four different sources. The growth rate is surface-reaction limited in region A and is mass-transport-limited in region B [3].](image)

2.4 Reactor Description

In this work, growth of polysilicon by LPCVD of silane was performed in a horizontal furnace reactor chamber. The Lindburg Sola Basic furnace features three
independent zone-controllers. The furnace is four feet in length. The hot zone of the furnace is three feet in length, beginning 6 inches into the furnace on both ends. The horizontal cylindrical axis of the furnace can accommodate quartz tubes of 8 inches in diameter however the quartz tube utilized in this system is 6 inches in diameter and five feet in length. The loading side of the furnace tube is sealed by means of a pressure differential between atmosphere and the reactor chamber. The cap assembly consists of a gasket and seal plate mounted concentrically around a quartz plug 7 inches in diameter extending approximately 1.5 feet into the furnace tube. Figure 2.2 shows the basic design of the system.

At the opposite end of the furnace tube, the vacuum tube tapers down to a quartz cylinder 1.5 inches in diameter. This cylinder extends beyond the body of the furnace tube where it is then coupled with a vacuum line. Below this vacuum port, a thermocouple well is fused into the furnace. The thermocouple well is a tube slightly under 3 feet in length and 2
cm in diameter. The thermocouple well protrudes into the interior of the vacuum chamber and ends in close proximity the end plug. The thermocouple well accommodates five type-R thermocouples embedded in a ceramic material that is capable of providing electrical insulation for the leads at high temperatures. A Keithley 740 scanning system thermometer is connected to a type-R thermocouple and correlates the voltage across the thermocouple to junction temperature and in turn outputs this value on its front display.

The vacuum system components existing outside the furnace chamber include an Alcatel vacuum pump, a pump inlet trap, a MKS type 252A exhaust valve controller, a Hastings thermocouple vacuum gauge, and an MKS Baritron vacuum gauge system.

The vacuum pump is connected to the vacuum chamber via the particulate trap and a steel vacuum tube. A line delivering dry N\textsubscript{2} to the pump is connected via the pump’s exhaust manifold. The purpose of this nitrogen gas line is to dilute the pump’s exhaust and also prevent silane gas from accumulating in the pump. The exhaust valve is incorporated into the main line, between the Hastings and Baritron vacuum transducers. The Baritron transducer is on the side of the reactor chamber while the Hastings T.C. transducer is on the side of the pump relative to the exhaust valve.

The Baritron vacuum gauge is interfaced with a MKS PDR-C-1B unit which correlates the voltage output of the transducer to the system pressure at the Baritron gauge. This output pressure is displayed on the front of the MKS unit. Additionally, the voltage output of the Baritron transducer is also provided to an MKS pressure controller unit. This unit is connected to the exhaust throttle and regulates system pressure at a desired value during a LPCVD growth.

The Hastings thermocouple pressure transducer indicates the pressure near the pump
inlet. For reliable operation, this pressure value must always be lower than that of the Baratron gauge while SiH₄ is sourced to the chamber. Or rather, when the exhaust value is fully opened, the pressure indicated by the Hastings gauge at a given flowrate determines the minimum deposition pressure at that particular flowrate. The typical system baseline pressure is approximately 65 mTorr.

Silane and nitrogen are available to the reactor chamber via a gas line that is connected to the front, or loading end of the furnace. A master gas control enables two Tylan 260 mass flow controllers, one each for nitrogen and silane.

Within the reactor chamber a quartz runner approximately 3 feet long rests as far back inside the furnace as possible. A quartz boat which serves as a sample platform in all experiments is supported by the runner. When under vacuum the boat rests in position slightly above the thermocouple well.

2.5 Deposition Procedure

Polycrystalline silicon films were deposited on two types of substrates for this work. The first type of substrate employed was commercially available Corning 7059 glass samples. The second type of substrate was (100) crystalline silicon wafers covered with a 100 nm thick thermally-grown dry oxide. Both types of substrates were subjected to the RCA or "standard" clean prior to their introduction to the reactor chamber. The RCA clean consists of immersion in a 1:1:5 NH₄OH:H₂O₂:H₂O solution heated to 80 °C for fifteen minutes, rinsing, a brief immersion in 50:1 diluted HF, subsequent rinse, and finally an immersion in a 1:1:6 HCl:H₂O₂:H₂O at 80 °C. The samples were removed, rinsed, and dried.

The LPCVD reactor was brought up to atmospheric pressure so that samples could be
loaded. In doing this, the exhaust throttle valve control was set to the completely closed position and 200 sccm of \( N_2 \) was directed into the reactor chamber. After approximately one minute the pressure within the chamber reached atmosphere and the cap was removed.

Using a push-rod, the runner was partially drawn out of the furnace tube to allow for substrate loading. Silicon wafers were mounted vertically in a quartz boat with the polished surface facing the gas stream source. Glass substrates bend and warp at temperatures used during these growths, and therefore, were required to lay flat on a silicon wafer which was placed across the boat. The boat and runner were then brought back into position, locating the substrate approximately in the center of the furnace hot zone.

The end cap was replaced and the exhaust valve was opened so that the system could once again pump down to low-pressure. The growth temperature was selected by setting the three furnace controls to the desired value. Temperature ramp-up required about 20 minutes.

Prior to deposition, the system was once again purged with 20 sccm nitrogen. Silane was then sourced to the reactor chamber by way of a mass flow controller. Silane flow rates were in the range 25-35 sccm throughout this series of experiments. Simultaneously with the sourcing of silane, chamber pressure was regulated to the desired value via the exhaust throttle control. Selected deposition pressures were varied in the range of 200-500 mTorr. Once the growth was completed, the silane source was closed and the exhaust throttle fully opened. The system returned to its baseline pressure. The system was then purged finally with nitrogen for five minutes. The exhaust throttle was set to closed, and the reactor was brought up to atmospheric pressure. The end cap was removed and the samples are removed.
2.6 Phosphorus Diffusion

Various samples were doped with phosphorus to modify electrical characteristics of the polysilicon [9]. Phosphorus was not grown into the films \textit{in situ}, but rather was diffused into the films using planar source wafers. The planar diffusion sources used were commercially available PH-950 type manufactured by Saint Gobain ceramics. The source wafers were entirely composed of silicon pyrophosphate, \(\text{SiP}_2\text{O}_7\). When heated to diffusion temperatures \(\text{P}_2\text{O}_5\) vaporizes from the source. This vapor deposits on the polysilicon forming a dopant glass. This glass undergoes a further chemical reduction leaving \(\text{SiO}_2\) and phosphorus.

Polysilicon samples were cleaned prior to phosphorus diffusion using the RCA process. The samples were placed with the side to be doped directly facing the source wafers on both sides in a quartz boat. The boat was then pushed into the 900°C diffusion furnace over the course of five minutes. The furnace ambient was 100% \(\text{N}_2\) flowing at 2 slpm. The samples were soaked for 20 minutes before being pulled from the furnace at the same rate they were introduced into it.

The samples were removed from the boat upon cooling and immersed in HF buffered oxide etch for 2 minutes to remove any un-reacted dopant glass.
Chapter 3: Characterization Techniques

3.1 Thickness Measurements

3.1.1 Nanometrics Model 210 Nanospec® Film Measurement System

The thicknesses of polysilicon films grown on silicon substrates were measured using a Nanospec® 210 film thickness measuring system. This system features an integrated spectrophotometer which can measure sample reflectance in the wavelength range of 370 nm to 800 nm. The Nanospec then employs a curve-fitting algorithm to determine the film thickness. For measurement of polysilicon films, the program specifies that the films are to be deposited on a silicon wafer covered with an oxide 100 nm thick. The instrument can accurately measure polysilicon films which are between 55 nm and 1,000 nm.

3.1.2 UV/VIS/NIR Reflectance

A separate spectrophotometer was used to determine the thickness of films deposited on glass and estimate the band gap of the material by means of absorption. The spectrophotometer used to make these measurements was manufactured by Perkin-Elmer and was interfaced with a PC running the UVWinLab® program. Parameters such as reflectance, transmittance, and absorption are measured by means of a light beam, which originates from a tungsten-halogen light source, and is then split into two beams. One beam is incident upon the sample, while the other is used as a reference. These two beams are then compared after the interaction with the sample. The measurement range was for wavelengths between 400 nm and 2,000 nm.

Reflectance measurements serve as the basis for thickness determination due to the
interference patterns caused by reflection of the beam off of two interfaces, namely the front and under surfaces of the polysilicon film. Photons of certain wavelengths interfere constructively while other wavelengths interfere destructively resulting in relative minima and maxima based on the film thickness and refractive index. Figure 3.1 provides a typical two-interface reflection pattern. Notice the oscillatory behavior diminishes at the lower wavelengths as the signal from the back interface is absorbed.

![Percent Reflection vs Wavelength](image)

**Figure 3.1 Percent reflectance vs. wavelength for thickness calculations**

Sample thickness may be calculated by Equation 3.1 [10]. Here $n_1$ and $n_2$ are the refractive index of the film at $\lambda_1$ and $\lambda_2$ respectively. The refractive indices are correlated with sample crystallinity based on data available at Ioffe Physico-Technical Institute [11].

\[
t = \frac{\lambda_1 \lambda_2}{4 (\lambda_1 n_2 - \lambda_2 n_1)}
\] (3.1)
3.2 Optical Band Gap

The Perkin-Elmer spectrophotometer can also be used to measure other optical sample characteristics. If the sample’s reflectance, absorbance, and thickness are known, the absorption coefficient may be determined from Equation 3.2 [10].

\[
\alpha(\lambda) = \frac{2.303 \cdot A(\lambda) - \ln \left( \frac{1}{1 - R(\lambda)} \right)}{t}
\]  

(3.2)

The photon energy at which the absorption coefficient exceeds \( \alpha = 10^4 \, \text{cm}^{-1} \) is commonly referred to as the \( E_{04} \) energy or optical gap, and provides an estimation of the semiconductor band gap. The basis for this estimation is the assumption that absorption must occur between extended states when the skin depth is shallow.

Absorbance was measured over the wavelength range of 400 nm to 2,000 nm and the absorption coefficient \( \alpha \) was then calculated. Figure 3.2 shows a typical plot of the absorption coefficient versus wavelength for the same film reference in Fig. 3.1 above. The oscillation of the absorption coefficient at low photon energies is indicative of regions where strong reflection is taking place. Of course, care must taken to accurately determine the optical band gap in these regions.
3.3 Raman Spectroscopy

Raman spectroscopy was employed for the purpose of determining the amorphous versus crystalline volume of the polysilicon films. To perform the Raman measurements, an inVia® Reflex Raman microscope manufactured by Renishaw was utilized. The system’s excitation laser operated at a wavelength of 488 nm (2.54 eV).

Raman spectroscopy makes uses of inelastic scattering. Photons impinge on atoms in the sample and are either absorbed or reflected by the sample elastically. However, certain photons interact with the sample inelastically by being absorbed and promoting atoms in the material to a raised ‘meta-state’. Phonon interactions during this meta-state cause a shift in photon energy as the photon is re-emitted as the meta-state collapses. Phonon interactions can either shift the energy of the emitted photons down (Stokes scattering) or up (anti-Stokes scattering).
scattering).

This interaction with the transverse- and longitudinal-optical phonon in crystalline silicon manifests as a Lorentzian peak sharply centered around $521 \text{ cm}^{-1}$ [12]. Amorphous silicon is not as an efficient Raman scatterer and exhibits a broad Gaussian peak at around $480 \text{ cm}^{-1}$. The Raman spectra of mixed-phased silicon is therefore a convolution of both of these modes [13].

Using numerical techniques, the overall response may be deconvolved into the respective crystalline and amorphous functions. The mathematical package OriginPro® 7.0 was used to accomplish this task. To perform this analysis, the baseline response was first subtracted from the overall response. This operation effectively normalized the crystalline response relative to the amorphous response. The baseline value was set in Origin by selecting a number of points in regions where the Raman spectra was relatively constant. Origin then calculated the resulting baseline and subtracted it from the Raman spectra. The peak-fitting feature was then used to fit a Lorentzian peak at $521 \text{ cm}^{-1}$ and a Gaussian at around $480 \text{ cm}^{-1}$ based on the deconvolution of the spectra. Figure 3.3 depicts a typical spectra.
Figure 3.3 Deconvolution of Raman spectra for estimating crystalline volume fraction. The crystalline peak is centered at 520 cm\(^{-1}\), whereas the amorphous peak is 480 cm\(^{-1}\). This sample, grown at 200 mTorr and 600°C is 92% crystalline by volume.

It has been demonstrated by R. Tsu et al that the crystalline volume fraction may be estimated by the following relationship given in Equation 3.3 [9,13].

\[
Crystalline\text{Fraction} = \frac{I_c}{I_c + 0.8 \cdot I_a}
\]

(3.3)

Here \(I_c\) and \(I_a\) are the intensities of the crystalline and amorphous peaks respectively. The factor of 0.8 is an approximation based on a variation between momentum exchange between excitation photons and amorphous material versus that of crystalline material.

3.4 X-ray Crystallography

X-ray crystallography measurements were taken to examine relationships between
deposition temperature to lattice structure and grain size [13,14]. The x-rays are fluoresced from a copper source that is bombarded with high energy electrons. The x-rays are of a wavelength comparable to the lattice spacing of crystalline sample. X-rays primarily interact with atoms’ electron orbitals and elastically scatter. Some x-rays are scattered from the first lattice plane; others will penetrate further and subsequently will be reflected from underlying planes. Reflections from these planes interfere with one another constructively or destructively. The condition for constructive interference is given by Bragg’s law and is dependent upon lattice spacing \( d \), wavelength \( \lambda \), and incident angle \( \theta \). This relation is known as Bragg’s law.

\[
n \cdot \lambda = 2d \cdot \sin(\theta) \tag{3.4}
\]

Grain orientation may be inferred by scanning the x-ray source and detector over a range of angles. As the Bragg condition is met for specific grains within the polysilicon film, an intensity peak will appear and reveal the orientation of those grains. Furthermore, the average grain size may be determined by analysis of the peak shape and intensity.

After the x-ray data was recorded, the data was imported into an x-ray diffraction analysis program called JADED®. JADE deconvolves the individual peaks after the baseline has been subtracted. The peak deconvolution yields the FWHM value of the peak. Equation 3.5 is Scherer’s formula and may be applied to calculate the estimated grain size [15].

\[
d = \frac{0.9 \lambda}{\beta \cdot \cos \theta} \tag{3.5}
\]

In Equation 3.5, \( d \) is the grain size, \( \beta \) is the FWHM, \( \lambda \) is the x-ray wavelength, and \( \theta \) the angle of incidence.
Lattice orientations <111>, <220>, and <311> were compared over a range of temperatures. The positions of these grain peaks are located at angle \(2\theta\) equal to 28°, 47°, and 56° respectively. The <220> peak is used to determine <110> growth [13]. Figure 3.3 is an example of x-ray diffraction from a sample grown at 675°C at a pressure of 200 mTorr.

![Count vs 2θ](image)

**Figure 3.3** X-ray intensity vs. \(2\theta\). Peaks indicate Bragg angle interception with grains of particular orientation.

### 3.5 Resistivity

One of the many virtues of polysilicon is its versatility as an electrical component in integrated circuits. The resistivity of polysilicon can vary over several orders of magnitude depending on its crystallinity and doping concentration[5]. Therefore a method of measuring the resistivity of polysilicon films is useful because the resistance of circuit components may then be geometrically determined and designed [14]. This knowledge is also required for MOS gate design.
The four-point probe allows one to measure I-V characteristics of films without having to take the probe-sample contact-resistance into account. Four contacts are arranged in a line with equal spacing between each contact. The outer pair of contacts are connected to a current source. The inner pair of contacts are interfaced with a voltmeter. As the contacts are lowered onto the sample and current is sourced, the current will spread out into the sample and then be collected symmetrically by the other probe. The flux of current within the sample can be derived from the geometry of the sample through superposition. Given the very high input impedance of the voltmeter probes, the potential measured by the voltmeter will be very close to the potential at the point of contact between the sample and the probe. Figure 3.4 shows the basic four-point probe arrangement.

![Figure 3.4 Four-point probe schematic diagram.](image-url)
If the sample is approximated as extending infinity in the horizontal plane, but of finite thickness \( t \), the resistivity of the sample may be deduced from Equation 3.6 [14].

\[
\rho = 2 \cdot \pi \cdot s \cdot \left( \frac{V}{I} \right) \left\{ \frac{2s}{t} \cdot \ln \left[ \frac{\sinh \left( \frac{t}{s} \right)}{\frac{t}{2s}} \right] \right\}^{-1}
\]

(3.6)

Here, \( s \) is the probe spacing and \( t \) is the film thickness. Once, the resistivity has been determined, sheet resistance may be calculated—the units of which are conventionally called ‘ohms per square’ (\( \Omega/\square \)) [3].

\[
R_s = \frac{\rho}{t}
\]

(3.7)

The specific four-point probe arrangement used to perform these measurements was comprised of a Signatone® commercial four-point probe platform having a probe separation of 0.1016 cm. The current source was a Keithley 220 programmable current source; the voltmeter was a Fluke 8842A multi-meter. The current source and the voltmeter were connected to a computer DAQ system via a GPIB interface. The sampling of I-V data, and the computation of resistivity, sheet resistance, and correction factors were greatly expedited through use of software developed by Gary Tuttle.
Chapter 4: Results and Discussion

4.1 Deposition Rate Trends

Twenty-four films were grown to investigate the affects of temperature and pressure on growth rate. These depositions were performed at pressures of 200 mTorr, 300 mTorr, 400 mTorr, and 500 mTorr. At each pressure value, growths were done at temperatures of 575 °C, 600 °C, 625 °C, 650 °C, 675 °C, and 700 °C.

Deposition rate is expected to increase with increasing pressure.\cite{5,7,16,17,18} This trend is most evident at lower temperatures. However, at higher temperatures the affects of silane depletion become more pronounced and the curves begin to approach a common growth rate.

In Fig. 4.1, one observes that the affect of depletion is most pronounced in low-pressure/high-temperature regions \cite{19}. Unfortunately, these are the regions best suited for the growth of highly crystalline films.
Nevertheless, films grown at 300 mTorr at 675°C have been shown to have very high crystallinity and uniformity, without showing high depletion in the center of the reactor. Three identical samples were prepared under these conditions and showed thicknesses which were repeatable within 10%.

Figure 4.2 typifies the transition region between mass-transport and surface-reaction rate limited reactions. The deposition rate is plotted versus 1/kT. Fitting an exponential curve to the right-hand side of Fig 4.2 gives an activation energy approaching $-E_a = -1.6$ eV [5].
4.2 Band Gap Results

The optical gap was measured for eight films grown on glass substrates. Six of these films were grown at a pressure of 200 mTorr at temperatures between 575 °C and 700 °C at 25°C increments. Three were grown at a single temperature of 675°C while regulating the pressure to 200-, 300-, and 400 mTorr.
4.2.1 Effect of Deposition Temperature

The band gap varied greatly with deposition temperature. The film grown at the low temperature of 575 °C exhibited the highest $E_{04}$ energy. Band gap decreased steadily as deposition temperature increased. The film with the lowest $E_{04}$ energy, $E_{04} = 1.46$ eV, was grown at the highest temperature.

![Band Gap vs Deposition Temperature](image)

Figure 4.3 Band gap vs. deposition temperature for samples grown at 200 mTorr.
4.2.2 Effect of Crystalline Fraction

The observation that band gap decreased with increasing deposition temperature is almost certainly due to the high crystallinity of the films grown at higher temperatures. Well defined energy bands arise in semiconductors due to the periodic nature of their crystalline lattice. As the lattice becomes more disordered the energy required to promote carriers is increased. As a result, the band gap is expected to decrease with increasing film crystallinity [20, 21].

It was observed that for films deposited in this experiment, the band gap lowered as the crystalline fraction of the film increased. Here a difference of 15% in crystalline volume correlated to a 0.42 eV drop in band gap.

![Band Gap vs Crystalline Fraction](image)

Figure 4.4 Band gap vs. crystalline volume fraction for samples grown at 200 mTorr.
4.2.3 Effect of Pressure

Finally, the observed change in band gap with respect to pressure is negligible for the films grown for these experiments. This uniformity is due to the relatively high deposition temperature of 675°C. Each film grown at this pressure exhibits a high degree of crystallinity regardless of pressure as given in Fig. 4.5.

<table>
<thead>
<tr>
<th>Deposition Pressure</th>
<th>200 mTorr</th>
<th>300 mTorr</th>
<th>400 mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap</td>
<td>1.47 eV</td>
<td>1.50 eV</td>
<td>1.50 eV</td>
</tr>
</tbody>
</table>

Figure 4.5 Band gap for films deposited at 675°C at different pressures

4.3 Raman Analysis

Raman spectroscopy data taken on 24 samples were taken and deconvolved in OriginPro®. The crystalline fraction of each sample was determined by comparison of the relative intensity of the amorphous and crystalline peaks. The crystallinity of the samples are recorded in Fig. 4.6 and plotted in Fig. 4.7. These results correlate well with the findings of others [5,9,12,17,18].

<table>
<thead>
<tr>
<th>Temp/Pressure</th>
<th>200 mTorr</th>
<th>300 mTorr</th>
<th>400 mTorr</th>
<th>500 mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>575 °C</td>
<td>84.4%</td>
<td>19.4%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>600 °C</td>
<td>91.7%</td>
<td>91.6%</td>
<td>90.1%</td>
<td>93.1%</td>
</tr>
<tr>
<td>625 °C</td>
<td>97.5%</td>
<td>95.3%</td>
<td>94.2%</td>
<td>93.6%</td>
</tr>
<tr>
<td>650 °C</td>
<td>98.9%</td>
<td>98.1%</td>
<td>98.2%</td>
<td>98.1%</td>
</tr>
<tr>
<td>675 °C</td>
<td>99.8%</td>
<td>99.7%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>700 °C</td>
<td>99.1%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Figure 4.6 Table showing percent crystalline volume for films grown a various temperatures and pressures.
Figure 4.7 Plot of percent crystalline volume vs. deposition temperature for various pressures.

Of the films grown at the lowest temperature of 575 °C, only the films grown at 200 mTorr and 300 mTorr exhibited any degree of crystallinity. The 200 mTorr film was predominantly crystalline at 84% volume while the 300 mTorr film was only 19% crystalline. However, at the next temperature set. The affect of deposition pressure on overall crystallinity is reduced as the crystalline fraction exceeds 90% at all pressures. This trend continues and by 675 °C the amorphous peak is no longer present and films are 99% regardless of pressure.

This result agrees well with the findings of Kamins and those of Modreanu, et al. who have shown the transition boundary between amorphous versus crystalline films[5,17]. The minimum pressure at which crystalline films may be deposited has an exponential
dependence with pressure. The reason for this ‘leveling’ is that crystalline deposition depends mostly on the ability for atoms to travel and arrange themselves along the surface. The average distance that an atom may travel is known as the surface-diffusion length. Equation 4.1 is an approximate formula for the diffusion length [16]. While RD, the deposition rate, is also positively correlated with increasing temperature, the exponential relation to temperature dominates the expression. The activation energy here is that which is associated with surface diffusion and has been found to be around 4 eV [16].

\[
L \approx \sqrt{Dt} \approx \frac{1}{\sqrt{R_D}} \exp \left( -\frac{E_a}{2kT} \right)
\]  

(4.1)

Physically, the surface diffusion length is increased at higher temperatures. The greater the distance that an atom may travel over the surface, the greater the chance that atom will be captured by low-energy (high bonding potential) sites in the lattice. These sites are typical of atomic layer edges, corners, and trenches where the atom has opportunity to form multiple bonds and decrease overall free energy of the film, resulting in a highly-ordered, crystalline structure.

4.4 X-Ray Diffraction Analysis

X-ray diffraction was performed on five samples; each sample was grown at 200 mTorr and at intervals of 25°C at temperatures between 600 °C to 700 °C. X-ray analysis was performed to determine the presence and size of <111>, <220>, and <311> oriented grains. Figure 4.8 shows the measured grain size for these orientations for films grown at
At the lowest temperature of 600°C only the <220> grain orientation is discernable with the <111> and <311> peaks absent. These <220> grains are approximately 110 nm in size. The morphology changes however as temperature increases. At 625°C, <220> grains have doubled in size at 205 nm but <111> and <311> grains have also formed, these grains are smaller at 90 nm and 85 nm respectively. It is also important to note that the <311> grains are at their maximum size at 600°C and then decrease their contribution to the overall film volume. Modreanu has stated that this orientation is preferred in a fairly narrow pressure-temperature region from 580°C to 600°C at pressures in the range 75-750 mTorr [22]. The growth condition for the 600°C, 200 mTorr film fall in the center of this region and confirm this claim.

At higher temperatures the <111> grain size increases slightly to 93 nm at 700°C at
the expense of the $<311>$ and $<220>$ peak. Nonetheless the $<220>$ remains the dominant orientation[7].

4.5 Resistivity Trends

Prior to planar source diffusion, measurements of resistivity and sheet resistance were attempted. It was discovered that these films were essentially insulating. The current source was not able to source a current at the highest voltage compliance setting.

A film grown at a pressure of 300 mTorr at 675°C was then annealed for one hour at a temperature of 900°C was measured in order to determine if any change in crystal structure during the deposition would have a large impact on resistivity independent of the phosphorus doping. It was found that this film was essentially insulating also.

Twenty-four samples were then doped with phosphorus for 20 minutes at 900°C (not including a five-minute push and five-minute pull). The films were processed in two batches. The first batch were those films grown at 400 mTorr and 500 mTorr. Those films deposited at 200 mTorr and 300 mTorr were processed approximately 60 minutes later in order to ensure the PH-950 source wafers had cooled to room temperature.

The conductivity of the polysilicon films was much improved after the phosphorus deposition. Many of the films displayed resistivites nearly as low as 0.002 Ω-cm. Growth temperature and pressure did not seem to have a noticeably affect the final resistivity. These values are plotted in Fig. 4.9.
These resistivities are in agreement with previous work [5, 23], where it was reported that the minimum resistivity for phosphorus doped films is approximately $3 \times 10^{-3}$ Ω-cm for films deposited at temperatures near the lower end of this data [23]. This minimum resistivity increases somewhat. Films grown near 700°C are reported to have minimum resistivities approximately $4.5 \times 10^{-3}$ Ω-cm. Kamins reports a lower limiting resistivity for phosphorus ($4 \times 10^{-4}$ Ω-cm) for ion-implanted films that were subsequently annealed at 1,000°C.

It is thought that the number of electrically active phosphorus donors saturates at $2 \times 10^{20}$ cm$^{-3}$. Moreover, solid solubility is thought to limit the resistivity of films grown over large temperature ranges and deposition processes.

There were, however, two notable exceptions. Those films grown at 300 mTorr had higher resistivities than films which were grown at both higher and lower pressures. These
films had also grown at rates slightly higher than expected. However, these films were confirmed to be highly crystalline when grown above 625°C and no ready conclusion is drawn as to the cause of this deviation. Despite this deviation the resistivity of these films was still very much improved when compared to prior to the diffusion.

Another notable exception is three of four films which were grown are 575°C did not improve in conductivity after have been diffused. The likely cause for this is the amorphous structures of these films. These films contain a large amount of trapping centers that limit the number of carriers available for conduction.
Chapter 5: Conclusions

5.1 Film growth

The films grown in this series of depositions did follow trends formulated by other authors in a general sense. Indeed, deposition rate does increase nearly linearly with pressure. The deposition rate also varies exponentially with temperature with an activation of around 1.6 eV verified.

However, producing films of acceptable quality involved trading-off between various factors. When the silane pressure is raised to increased deposition rate, it is done so at the expense of film crystallinity. If temperature is increased to hasten film growth, silane depletion becomes significant enough that the deposition rate may actually decrease. Moreover, it is known that at low temperatures in the surface-reaction rate limited regime films may be grown that are very uniform. Nonetheless, the films at these temperatures have a much greater likelihood of being amorphous.

For this particular LPCVD system, the best films appear to grow well near pressures of 300 mTorr and temperatures around 675°C. These films grow quickly, are highly crystalline, and are more repeatable due to the limited effect of gas depletion.

5.2 Optical Properties

The variation in optical behavior between films deposited under different conditions clearly followed expected trends. The optical band gap always decreased with increasing film crystallinity. The variation of the optical gap with temperature follows as a corollary.
5.3 Crystallinity and Morphology

Raman spectroscopy provided the means to easily acquire knowledge of a film’s crystalline versus amorphous nature. With this tool available, one could readily observe the pressure-temperature regions in which amorphous films make crystalline transitions. For this particular LPCVD system, no semi-crystalline film could be deposited below 560°C. X-ray diffraction further enhanced understanding of the transitions occurring between grain orientations. Though the relative grain size did change over those peaks measured. The <220> exhibited the highest peak intensity over the entire range of temperatures.

5.4 Resistivity

Intrinsic films grown in this LPCVD system were highly non-conductive regardless of their crystallinity or growth temperature. The presence of grain boundaries have likely created trap states with capture most of the already few intrinsic free carriers. Annealing these films resulted in no noticeable effect. However, when these films were doped heavily with phosphorus they became respectably good conductors of electricity.

5.5 Future Work

To the end of better characterizing this LPCVD system, growths and experiments could be designed to determine mechanical parameters such as Young’s modulus. Or, sub-gap absorption measurements could be performed. Also, surface texture increases markedly upon crystallization. Attempt may be made to measure this change in roughness.
References


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Appendix: LPCVD Standard Operating Procedure

Initial Setup:

Open valves on the nitrogen dewar and nitrogen line located near the primary entrance of the clean room. Make certain that the liquid level of the nitrogen in the dewar is adequate for an extended run time. If level is below ¼, use another dewar. Furthermore, ensure the dewar and line pressure are at least 30 psi. Record these pressures.

Open nitrogen flowmeter valve and pump manifold, making certain that at least 10 scfh N2 is being delivered into pump for dilution purposes.

Note initial temperature set points and thermocouple outputs.

Note initial Baritron and the thermocouple vacuum values to ensure the LPCVD system is maintaining an adequate baseline vacuum. Typical values are 60 - 85 mTorr and should be under 100 mTorr.
System Loading:

Provided the system is already under vacuum pressure, the tube must be vented so that the cap may be removed and substrates subsequently loaded.

Power-on the Tylan 4-channel mass flow controller unit as pictured in Fig. A1.

Select channel 4 corresponding nitrogen gas.

Position the read/set toggle switch on the unit to the Set mode.

Adjust the channel 4 control knob to a value of 200 sccm N2.

Position the read/set switch to Read mode.
Close the exhaust vacuum valve by positioning the small black toggle switch on the MKS control unit to the downward **Close** position as pictured. *Note: this switch is only enabled when the valve mode control knob is set to the Open mark.*

Wait approximately 10 seconds for the exhaust valve to close. A light on the MKS control unit will illuminate when the valve has reached the closed position. Additionally, the indicated pressure of the Bartron vacuum gauge will begin to increase while the pressure indicated by the Varian thermocouple gauge will remain relatively constant.

Turn on the Master Flow Control Box by switching the large center switch to the upright position. This unit is pictured in Fig. A2.

![Figure A2 Master flow control box](image)

Turn on the nitrogen gas switch. Nitrogen gas is now being introduced into the vacuum tube. After approximately 20 seconds time the end cap will loosen and may be separated from the tube.

**Don** high temperature gloves and appropriate lab goggles.
Carefully pull the end cap assembly from the furnace and place it on the lower shelf of the adjacent stainless steel table, keeping the assembly a safe distance from contaminants and combustibles.

Using a quartz push-rod, draw out the quartz runner within the tube. The runner must be lifted slightly with the push run in order that its front and center cross bars have clearance over the internal thermocouple well tube and do not impact it during movement. Stop pulling once the front of the runner overhangs approximately 5 inches.

Again using a push rod, gently pull the wafer boat to the front of the runner as pictured.

Wafers may now be placed into the boat. Variables to consider are wafer positioning relative to the boat as well as each other, and whether the wafers will face away or toward the oncoming gas stream. A convention used in this system is that, regardless of the wafer spacing or polished side orientation, the wafer’s primary flat should be on top (twelve o’clock position).

Position the boat in the runner to the desired position.

Using the push rod, gently transport the runner all the way to the back of the furnace. Again the runner must be lifted slightly to clear the thermocouple well.

Lift the endcap assembly and gently guide it into the mouth of the furnace. The cap must be aligned properly with the furnace tube as pictured.

Open the exhaust valve by toggling the small black control switch into the open position while the endcap is held in the correct position. Once activated, the valve will be opened after around 10 seconds. When this happens the pump will bear down and the endcap will establish a seal.
Turn off the nitrogen switch on the Master Flow Control box. If desired, the operator may also turn off the power switch as no gas is required until the system has had adequate time to reach thermal equilibrium.

**Polysilicon Deposition:**

Adjust the three furnace set points to the desired value. Record this value.

Wait a period of no less than twenty minutes for the system to reach thermal equilibrium. The temperatures indicated by the Keithley thermocouple reader should also have stabilized.

Open the LPCVD silane and silane-in valves located within the exhaust plume as shown in Fig. A3.

![Silane valves within exhaust plume.](image)

Turn the silane pneumatic valve control, located on the exterior of the exhaust plume, 180 degrees to the on position.
Open the silane cylinder valve.

Ensure that the silane regulator is set below 10 psi. Record this value.
Record the pressure of the silane cylinder.

Turn the exhaust valve control knob to the S.S. or Auto position. Set the exhaust valve pressure control to 300 mTorr. Note: The control has an offset; therefore in order to regulate the system to a pressure of 300 mTorr the control should be set to a value of about 245 mTorr.

Select channel-3 on the Tylan Mass Flow Controller box for silane.

Position the read/set control to the Set position and adjust to 30 sccm.

Position the read/set control to the Read position.
Power on the Master Flow Control box.

Activate silane flow by flipping the SiH4 switch as pictured in Fig. A2.

At this point the pressure in the system will increase dramatically. The overpressure relays will stop silane flow until the system pressure drops again. This may happen for two or three cycles. However, the system should quickly stabilize at the set point thereafter.

Maintain silane flow for the desired duration of the polysilicon deposition.

Switch the silane switch on the Master Control Flow box to off once the deposition time has elapsed.

Open the exhaust valve by positioning the control knob to the open position. Re-verify the open/close toggle switch is still in the open position.

Allow the system to pump-out under a no flow condition for a 5 minute period.

Select channel-4 on the Tylan Mass Flow Controller box, corresponding to Nitrogen.

Position the read/set control to the Set position and adjust to 20 sccm.

Position the read/set control to the Read position.

Turn-on the nitrogen switch on the Master Flow control box. Nitrogen will now begin to purge the system. Allow this purging to continue at least 5 minutes.

At this juncture, close all silane valves in the same order in which they were opened as specified previously.
Unloading:

System is unloaded in the same manner as it was loaded.

Close the exhaust valve by toggling the control switch down to the closed position.

Increase the nitrogen flow to 200 sccm.

The endcap assembly will release from the tube.

Remove the endcap and draw out the runner and boat in a manner consistent with the loading procedure.

Allow the wafers time to cool before removing them with stainless steel tweezers. Place these on an appropriate surface so they may further cool.

Replace the endcap.

Open the exhaust valve to reestablish the seal between the endcap and the furnace tube.

Turn off the nitrogen flow and power to the Master Flow Control box.

Shut Down:

Reverify that all silane valves have been closed.

Turn off Tylan Mass Flow Controller box.

Close nitrogen dewar and line valves supplying the lab.