

Characterization of Silicon Dioxide Thin Film Deposition

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ABSTRACT

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Silicon dioxide (SiO_2) is useful in microelectronics, micro-fabrication and optics. It has traditionally been deposited through low-pressure chemical vapor deposition (LPCVD) at high temperatures (about 900 to 1000 °C). Various reactants have been used in this process, such as dichlorosilane and oxygen, or silane and nitrous oxide in different combinations. We explore the reaction of dichlorosilane and nitrous oxide in SiO_2 LPCVD by varying the temperature from 850 to 950 °C and the pressure from 0.30 to 1.05 Torr. Films with mirror-like surfaces are deposited in an ambient temperature of 900 °C, with a gas ratio of 3.33 parts nitrous oxide for every one part dichlorosilane, and at a pressure between 0.35 and 0.69 Torr, while pressures outside of this range result in foggy surfaces or no deposition. These results are in good agreement with previous work and indicate that careful control of pressure is necessary for depositing uniform films for use in optical applications.

Keywords: Chemical vapor deposition, silicon dioxide, thin films, dichlorosilane, nitrous oxide

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Chapter 1

Introduction

1.1 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a process for depositing a thin film of material on a surface through a chemical reaction of vapor phase reactants. It is not limited to highly controlled processes used in the laboratory or factory. Instead, CVD refers to any process where gaseous chemicals react and form a solid layer of material on a surface.

It is desirable that the thin films produced by CVD form through heterogeneous rather than homogeneous nucleation. In both cases volatile gases decompose and react to form new compounds. In heterogeneous nucleation, this reaction occurs on a surface and forms uniform structures. On the other hand, in homogeneous nucleation the chemical reaction occurs before the gases reach the surface, forming molecules of the new compounds which then collide and react with other molecules until finally reaching the surface. This form of nucleation tends to result in a less uniform layer than heterogeneous nucleation [1].

To better understand the difference between heterogeneous and homogeneous nucleation, consider an analogy with frost and snow [1]. Neither frost nor snow are products of chemical vapor

deposition, but their similarities and differences help to illustrate nucleation. Frost does not fall from the sky, but rather moisture from the air simply freezes on the ground and other surfaces. Snow, however, is moisture in the sky that has already frozen and stuck to other pieces of snow while falling to the ground and finally piles up on top of itself in fluffy heaps. Both are made of the same materials, but different conditions result in different forms of nucleation. The same principles apply to CVD. While both forms of nucleation are understood, the boundary between one and the other is still being studied.

Controlled CVD is frequently used in microfabrication and optics. Thin films deposited through CVD are often of high quality and uniformity, making them ideal for coating lenses or delicate nanoscale components. Because many objects can be placed in the same chamber and have material chemically deposited on them simultaneously without any loss of uniformity or quality, CVD processes lend themselves well to high-quality mass-production.

1.2 Silicon Dioxide Thin Films

Silicon dioxide (SiO_2) is used in applications across a wide variety of fields. It is found in computers, micromechanical systems, optical fibers, drinking glasses, ceramics, as an ingredient in foods, and as a film on lenses. In nature it is most commonly found as α -quartz, though it is plentiful in many other forms as well. In thin films, silicon dioxide tends to be amorphous rather than crystalline, resulting in somewhat different properties. Silicon dioxide in general is useful as a thermal barrier due to its low thermal conductivity, and also works well as an electrical insulator. The refractive index of SiO_2 , about 1.45, and its relative abundance make it a common choice for use in optics.

Because silicon dioxide can take so many forms and can have slightly different properties depending on the form it takes, it is important to understand how its properties change depending on how it is made. If that dependence is understood, then better devices can be made and more reliable

results can be achieved. My research focuses on developing a recipe for CVD silicon dioxide using dichlorosilane (SiCl_2H_2) and nitrous oxide (N_2O) that will minimize surface roughness without sacrificing deposition rate. I first determine appropriate ranges for process parameters (reactant ratio, pressure, and temperature) and then study how changing these parameters effects the surface roughness of deposited films.

1.3 Previous Work on Silicon Dioxide Thin Films

Silicon dioxide is made through a variety of reactions. One family of these reactions takes the form of $\text{SiCl}_x\text{H}_{4-x} + \text{N}_2\text{O} \leftrightarrow \text{SiO}_2 + \text{byproducts}$, where x is either 0 or 2; although oxidizers other than N_2O can be used. For example, in the year 2000 Klaus and George [2] studied the chemical vapor deposition of SiO_2 with silane (SiH_4) and water vapor as the reactants and ammonia as a catalyst. They found that they could deposit SiO_2 thin films at room temperature with the help of a catalyst to provide the energy necessary to overcome the reaction energy. Eleven years earlier, Chapple-Sokol and Gordon [3] experimented with depositing SiO_2 with dichlorosilane (SiCl_2H_2) and oxygen. Their research was conducted at atmospheric pressure and focused mainly on the effects of the substrate on the film. Watanabe, Tanigaki and Wakayama [4] worked with dichlorosilane and nitrous oxide as reactants in their study of the properties of SiO_2 thin films. Their research focuses on the chemical composition of the films, especially as related to chlorine impurities left over from the CVD reaction.

This work focuses on the same chemical reaction studied by Watanabe et al. [4], namely $\text{SiCl}_2\text{H}_2 + \text{N}_2\text{O} \rightarrow \text{SiO}_2 + \text{byproducts}$. We also use the same recipe parameters used by Watanabe et al. as a rough starting place. However, where Watanabe et al. focused on analyzing the chemical and physical properties of their thin films, we take a step back and instead focus on analyzing the parameters themselves. Rather than fixing all but one of the recipe parameters and then mea-

During the result of changing that one parameter, we vary a couple parameters independently and search for the combination that maximizes deposition rate while simultaneously minimizing surface roughness. Preliminary results agree with the recipe used by Watanabe et al., but also indicate that the parameters can be more finely tuned for smoother films or faster deposition.

1.4 Recipe

We found that with a dichlorosilane to nitrous oxide ratio of 1:3.33, and temperature of 900 °C, the best pressure for silicon dioxide deposition lies between 350 and 690 mTorr. Unfortunately, this research has not yet resulted in a more precise pressure corresponding to the smoothest films or fastest deposition. We have also not concluded a quantitative description of how changing pressure, temperature, or gas ratio affects the smoothness or deposition rate.

Our results do show that at a temperature of 900 °C, a 1:3.33 ratio of dichlorosilane to nitrous oxide, and pressures below 350 mTorr, little to no SiO₂ reliably deposits on the substrate. On the other hand, keeping all other parameters the same and increasing the pressure above 690 mTorr causes surface roughness comparable to the wavelength of light; that is, between 400 and 800 nanometers.

1.5 Overview

In the following chapters I describe the process we followed to determine our recipe for CVD silicon dioxide. In Chapter 2 I begin with a detailed description of the equipment used for sample preparation and analysis. That will be followed by a description of our experiment, including the problems we encountered and our solutions. I will pay particular attention to the problems we faced with rough films to conclude the chapter.

In Chapter 3 I restate the results of our project in more detail, beginning with a presentation of

the data we collected and followed by our interpretation of that data. I compare our recipe to others and comment on the comparative usefulness of our recipe. The chapter concludes with some ideas for future work related to our silicon dioxide recipe.

Chapter 2

Experiment

2.1 Experimental Design

Our experiment consists entirely of making and analyzing silicon dioxide thin films. We make the thin films in a low pressure CVD system designed and built by students at BYU. This system, along with other equipment used in analyzing the samples, will be described in greater detail in Section 2.2.

The deposition process begins by pumping down the furnace chamber to a pressure of about 50 mTorr using an Edward D-30 mechanical (roughing) pump. This pump runs continuously throughout the experiment so that all gas introduced to the chamber will flow through the chamber, resulting in dynamic rather than static CVD. While the chamber is initially evacuated, it is also heated to the target temperature: generally 900 °C. After the chamber is pumped free of air and has reached the desired temperature, we first introduce nitrous oxide followed by dichlorosilane gas, establishing a steady flow of both gases simultaneously. Then, after a predetermined amount of time, both gases are shut off, the chamber is allowed to cool and again pump down to about 50 mTorr. After the pressure has dropped below 50 mTorr and while the chamber is still cooling, we

periodically flow nitrogen gas into the chamber, allowing the pressure to rise above 2 Torr before shutting off the gas and dropping the pressure back below 50 mTorr. This is done in order to purge any remaining dichlorosilane or nitrous oxide from the chamber. After two or three cycles of flowing nitrogen gas, a constant flow is established in order to help the system cool down faster. We generally remove the samples from the chamber once the temperature has fallen below 250 °C.

We used parameters taken from Watanabe et al. [4] to initially determine what parameter ranges to investigate. During initial experimentation, using the exact same parameters as Watanabe et al., we did not achieve reliable depositions. Thus, we held the pressure at 0.6 Torr and varied the temperature from 850 to 950 °C until reliable deposits were observed. Once we determined the ideal temperature, we turned our attention to identifying ideal pressures.

Using a dichlorosilane flow rate of 33 sccm (standard cubic centimeters per minute), and a nitrous oxide flow rate of 100 sccm, we found that the steady state pressure of our system was just under the 0.6 Torr pressure we wanted. By decreasing the dichlorosilane and nitrous oxide flow rates each to one third of these values, we decreased the steady state pressure by an order of magnitude while keeping the gas ratio the same. This change allowed us to control the pressure more accurately with a butterfly valve during deposition. We attempted to deposit silicon dioxide at pressures ranging from 300 to 1100 mTorr.

Once we found the temperature, pressure, and flow rates that produce reproducible deposition, we began experimenting with coating multiple wafers in the chamber at once. We found, however, that having more than one silicon wafer in the chamber lead to rough deposition layers. The roughness was evident in the nonspecular reflection from the surface after deposition; or in other words, the samples appeared to be foggy. This and other problems related to roughness will be discussed in Section 3.2.

We also experiment with different deposition times in order to understand the deposition rate of our recipe. We measure deposition time from the moment the dichlorosilane and nitrous oxide

gases are introduced to the furnace chamber until the gas flow is shut off, just before the chamber is purged with nitrogen gas. It is important to note that this measure of deposition time includes the time it takes to reach the target pressure and ensure proper control. It does not include any deposition that might occur after the reactant gases are shut off and while the gas in the chamber is pumped out. Any deposition that takes place during that time should be negligible as the pressure in the chamber drops quickly as soon as the gas flow is shut off. This indicates that the reactants are quickly evacuated from the chamber and little deposition is likely to occur.

We analyze our samples using ellipsometry, electron microscopy, x-ray energy dispersive spectroscopy, and atomic force microscopy (AFM). We use ellipsometry in order to measure the thickness of the films, as well as their indices of refraction. Ellipsometry also gives us an indication of how rough the films are. Electron microscopy allows us to look at the structures causing roughness on our samples. We analyze the chemical composition of our samples with x-ray energy dispersive spectroscopy and verify our roughness measurements with AFM. These techniques will be explained in greater depth in Section 2.2.

2.2 Equipment

2.2.1 CVD System

Our deposition was done in a chamber designed and assembled by students. As you can see in Fig. 2.1, we used a mechanical roughing pump to bring our deposition chamber down to the desired pressure. Our reaction of dichlorosilane and nitrous oxide results in silicon dioxide and various noxious gases. We protect the roughing pump from all of these byproducts with a trap. Over time the trap clogs, limiting how well the pump can evacuate the system, thus requiring periodic cleaning or replacement.

The gas is introduced to the system through a series of valves and controlled by mass flow

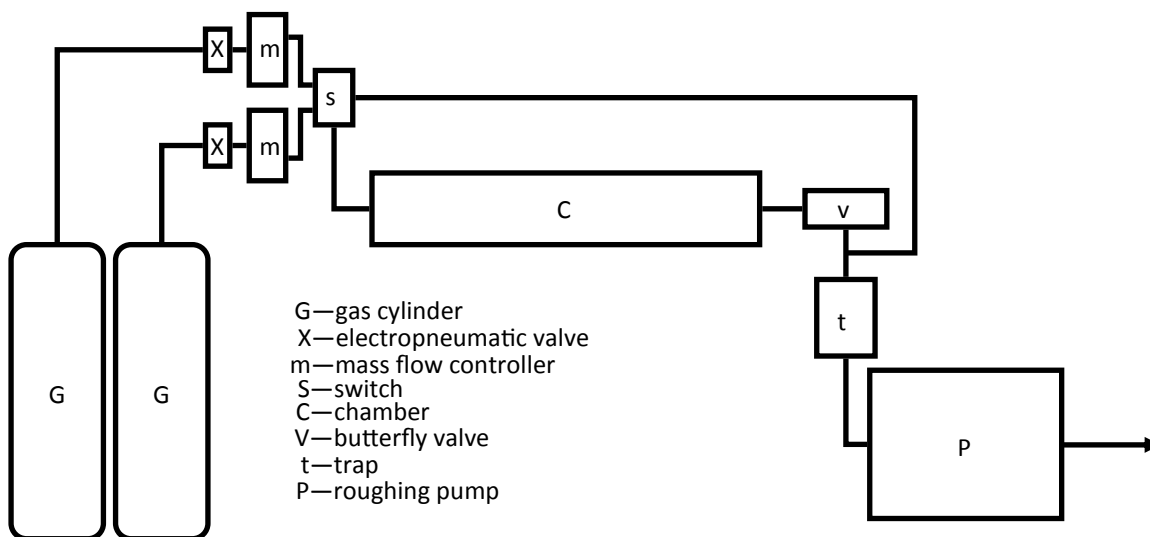


Figure 2.1 Schematic of our CVD system. Gas flows from left to right, the arrow on the right indicating exhaust. Note in the schematic that the two gases come together at the switch before the chamber. This is a simplification for the sake of clarity. In the actual system, the gases are kept separate until they reach the deposition chamber or are routed into the bypass line.

controllers. Electropneumatic valves allow us to open and close the gas lines with the flip of a switch. These valves come before the mass flow controllers in order to provide a reliable safety switch to stop gas flow in the case of an emergency. The mass flow controllers allow the gas flow rate to be controlled to within one standard cubic centimeter per minute. After passing the pneumatic valves and the mass flow controllers, we direct the gas either into the furnace or through a bypass line that reconnects just before the trap. This allows us to more accurately measure the deposition time of our samples. As soon as the gas is switched from the bypass to the furnace line we can begin measuring the deposition time, and then we end the deposition time when the gas is sent back through the bypass line. There may still be residual gas in the chamber when the gas is diverted to the bypass line, but the deposition time measurement is standardized in this way.

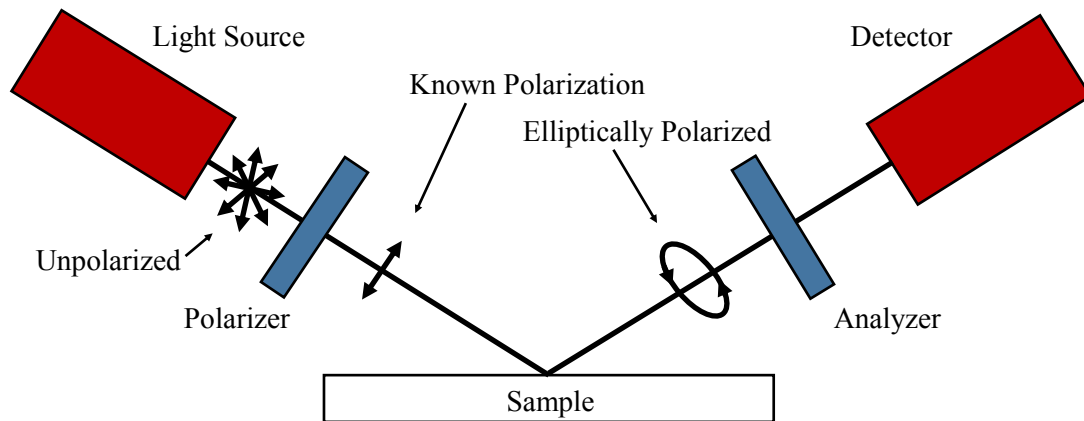


Figure 2.2 Simplified ellipsometric setup. Light passes through a polarizer and then reflects off the sample. The reflection changes the polarization and phase of the light. The analyzer measures the new polarization and phase.

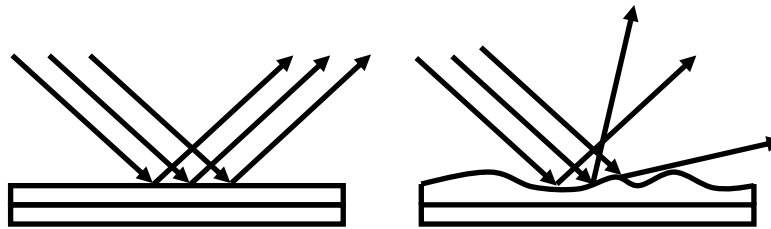


Figure 2.3 When light reflects off of a surface that is smooth compared to the wavelength of the light, it reflects specularly, as shown on the left. This results in a mirror-like surface. When the surface becomes too rough, the reflected rays are no longer all reflecting in the same direction as seen on the right.

2.2.2 Ellipsometry

Our film thicknesses and optical properties were measured primarily through ellipsometry. See Fig. 2.2 for a basic diagram of how an ellipsometer works. An ellipsometer does not directly measure the index of refraction or the thickness of a thin film. Polarized light with a known phase and polarization is reflected off of the sample and into an analyzer. The light at the analyzer is compared to the original light emitted, and the change in the light's polarization and phase is calculated. We can then fit this polarization and phase data to theoretical models, such as the Cauchy-Schwartz or Lorentz models, in order to measure the film's thickness and index of refraction indirectly.

This method of measuring thickness and the index of refraction depends strongly on how light reflects off of the film's surface. In order to get accurate data most of the light from the source needs to make it to the analyzer. This means that we need to have mostly specular reflection off the surface of our film. Specular reflection is the ideal reflection of light or other waves from a surface where the angle of incidence of the incoming waves from one direction equal the angle of reflectance of the reflected waves, as with a mirror. A rough surface results in some nonspecular reflection, and the more rough the surface is, the more it will scatter light. If the surface is very bumpy then light coming in from a single direction will reflect in many different directions, as depicted in Fig. 2.3. Therefore, if our film is not very mirror-like, a lot of the light is scattered away from the analyzer and we are unable to collect good data. Thus the surface of our film needs to be smooth on the order of the wavelength of light used to measure it. We had the ellipsometer scan through wavelengths from about 700 nm down to about 350 nm, so if our samples had rough surfaces where the bumps were fractions of microns in size, that would be too big and our films could not be measured accurately. This problem with roughness will be discussed in more detail in Section 3.2.

2.2.3 Scanning Electron Microscope

We used a scanning electron microscope (SEM) to image the surface of our samples and examine the structures causing surface roughness. The SEM allows us to capture images with nanometer resolution. The sample pictured in Fig. 2.4 is one example of the rough surfaces we deposited. The figure depicts a square area, about 10 μm on a side, dotted with particles about a micron in size. These particles are as big, or bigger, than the wavelength of visible light and thus cause nonspecular reflection. The SEM image also shows that the particles are fairly evenly distributed and lying on a smooth, even surface. This and other similar images (not represented here) indicate that when our deposition results in rough surfaces, we are probably not even depositing a thin film,

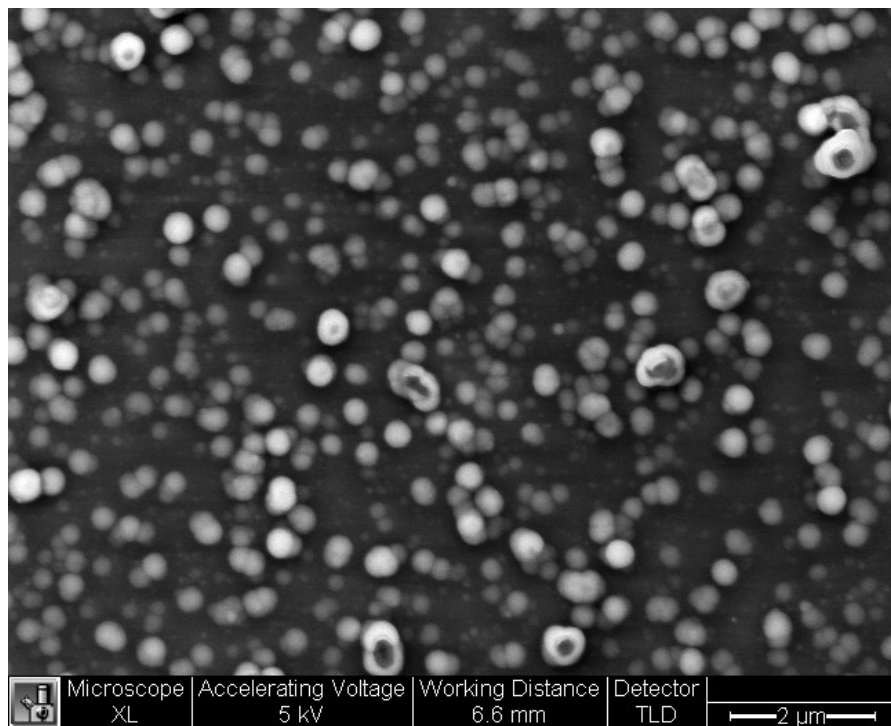


Figure 2.4 SEM image of an SiO₂ thin film. Notice the scale in the bottom right corner. This image shows surface roughness on the order of a micron.

but rather a speckle pattern of SiO₂ particles on top of the silicon wafer: not unlike the popcorn speckle used to finish the ceilings in old homes.

2.2.4 X-ray Energy Dispersive Spectroscopy

We also used the SEM to study the chemical composition of our thin films through x-ray energy dispersive spectroscopy. An SEM creates an image by accelerating electrons in a narrow beam and focusing that beam on the surface. Those electrons collide with the surface material, and by detecting and analyzing the electrons that get scattered, a digital image is formed. However, the accelerated electrons also excite electrons bound to the atoms on the sample's surface. When those excited electrons escape from the atom, they leave behind a hole that another bound electron in a higher energy state can decay into, releasing an x ray in the process. These x rays are specific to the type of atom involved because they are directly related to the energy levels of the atom. By analyzing the x rays being emitted we identify the elements present in the film as well as their relative abundance.

Spectroscopic data from our films verify that our deposition is pure silicon dioxide and not contaminated with other chemicals left in the film. Because we are depositing silicon dioxide with dichlorosilane and nitrous oxide, we would expect chlorine or nitrogen as possible contaminants. However, this analysis identifies every transition excited by the electron beam and thus allows us to identify any other contaminants in our deposition chamber. The software used to analyze the spectroscopic data automatically labels peaks with their corresponding element, but also allows for manual entry. We present a typical example of spectroscopic data from our thin films in Fig. 2.5, where the software automatically labeled the carbon, oxygen, and silicon peaks. The chlorine label was added manually to show where any x rays from chlorine atoms would appear. The lack of a peak above background noise indicates that no chlorine is present in the film (<0.1%). Nitrogen is not labeled in the figure, but if a nitrogen peak were present it would be located between the carbon

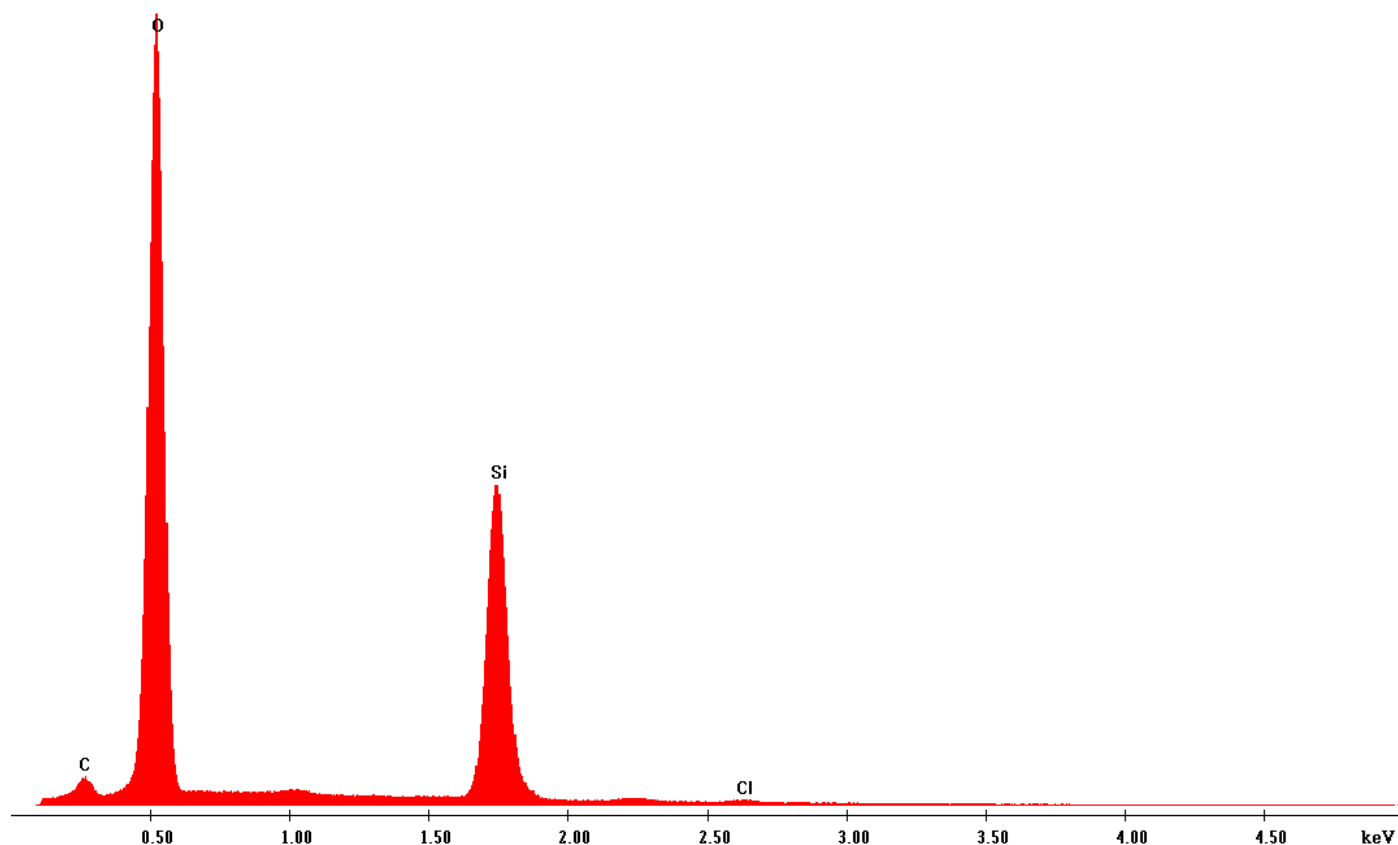


Figure 2.5 Example of spectroscopic data gathered from the same sample pictured in Fig. 2.4. The vertical axis is simply the number of x rays detected, and so its scale is unimportant; rather the relative heights of the peaks are what matter. However, because each atom is different and will emit x rays at different rates when excited by the same electron beam, the direct ratio of the peak heights is only qualitatively helpful.

and oxygen peaks. It should be noted that trace amounts of carbon were present on the sample. This may be adventitious contamination.

2.2.5 Atomic Force Microscopy

While the SEM provides greater insight into the composition and structure of our samples, atomic force microscopy (AFM) offers detailed, quantitative data about our films' roughness. Rather than using the reaction of electrons colliding with the sample to build an image, AFM physically traces the topographical contours of the surface.

There are different techniques for making AFM measurements. We use a technique called tapping mode in which a cantilever vibrates above the surface and an extremely small tip, less than a nanometer wide, attached to the end of the cantilever is allowed to tap the surface of our sample. Detecting a laser reflected off the end of the cantilever measures the cantilever's motion specifically to identify whether or not the tip is making contact with the surface. As the cantilever vibrates we scan it across the sample, and using a feedback loop a computer raises and lowers the cantilever so the tip continues to tap the surface without imparting excessive force. The position of each tap relative to a fixed coordinate system plots the contours of the surface. We then calculate the average roughness over the area measured and take a Fourier transform of the data for spectral analysis. Thus AFM provides more quantitative data about the roughness of our surface than the SEM.

Chapter 3

Results and Conclusions

3.1 Experimental Results

Through the methods described in Chapter 2 we determined the following parameters for CVD silicon dioxide using dichlorosilane and nitrous oxide: a temperature of 900 °C, a ratio of 3.33 parts nitrous oxide for every one part dichlorosilane, and a pressure between 0.35 and 0.69 Torr. Due to the relatively few samples we made that could be measured with ellipsometry we cannot conclude anything about how changing the parameters effects the index of refraction or deposition rate; thus, our results and conclusions focus on roughness. As can be seen in Table 3.1, every sample made at pressures greater than or equal to 0.69 Torr exhibited surface roughness on the same order of magnitude as the wavelentgh of visible light: 10^2 nm. Meanwhile, the sample made at a pressure of 0.35 Torr did not result in any deposition at all.

To be clear, the roughness layer data presented in Table 3.1 is not the same measure of roughness treated in sections 2.2.2 and 2.2.5. The measure of roughness given in the table is taken from ellipsometry and refers to a layer in the model used to find the overall thickness of the film. The model is composed of various layers, including the substrate, the thin film itself, transition layers,

| Sample Number | Pressure (Torr) | Flow Rates | | Time (min) | Roughness Layer (nm) |
|---------------|--------------------|--|----------------------------|---------------|-------------------------|
| | | SiCl ₂ H ₂ (sccm) | N ₂ O (sccm) | | |
| 140509a | 1.05 | 30 | 100 | 20 | |
| 140528b | 0.69 | 30 | 100 | 10 | |
| 140509d | 0.67 | 30 | 100 | 35 | 2.825 |
| 140509c | 0.65 | 30 | 100 | 25 | 3.21 |
| 140604a | 0.35 | 10 | 33 | 45 | |

Table 3.1 Representative data from thin film samples organized by pressure. The roughness layer refers to a thickness as found through ellipsometry rather than an average roughness as described in sections 2.2.2 and 2.2.5. Samples without a roughness layer entry were either too rough to measure by ellipsometry, indicating an average roughness on the order of 100 nm, or resulted in no deposition at all. Note the large gap in pressure between sample 140509c and 140604a. More samples made at pressures between 0.65 and 0.35 Torr are needed to better identify the lower limit of pressure.

and a surface layer of roughness. The roughness layer is really a simple model composed of 50 percent deposited material and 50 percent void; roughly replacing a surface of peaks and valleys with a smooth layer that is not solid. The roughness given in Table 3.1 is the thickness of the model's roughness layer.

3.2 Roughness

As was mentioned in Chapter 1, we ran into problems with film roughness during our experiment, and that led us to conjecture about the possibility of homogeneous nucleation taking place in our deposition. As our experiment focused on finding a recipe for silicon dioxide chemical vapor deposition and not on probing the boundary between homogeneous and heterogeneous nucleation, we cannot make any strong claims about the latter. However, if it could be shown that the roughness of our samples deposited at higher pressures was due, at least in part, to homogeneous nucleation, then our data could help to understand that boundary. It would indicate that the transition from homogeneous to heterogeneous nucleation takes place at almost 0.7 Torr and 900 °C, at least for the reaction of dichlorosilane and nitrous oxide. It should be made absolutely clear, however, that the roughness of our films could be due to other factors, either in whole or in part, and that further research needs to be conducted to truly make any conclusions.

The mound-like structures we found on each surface, such as depicted in Fig. 2.4, are one reason to suspect homogeneous nucleation as a source of roughness. As can be seen in Fig. 3.1, there are patterns in the deposition that indicate directions of gas flow. These patterns are another reason to suspect that deposition occurred through homogeneous nucleation. The mounds on the surface are reminiscent of snowflakes sticking to your windshield and the flow patterns are similar to the way snow piles up more in some places than others based on the way the wind is blowing. However, as was stated in Chapter 1, the analogy to snow is not perfect and other factors could

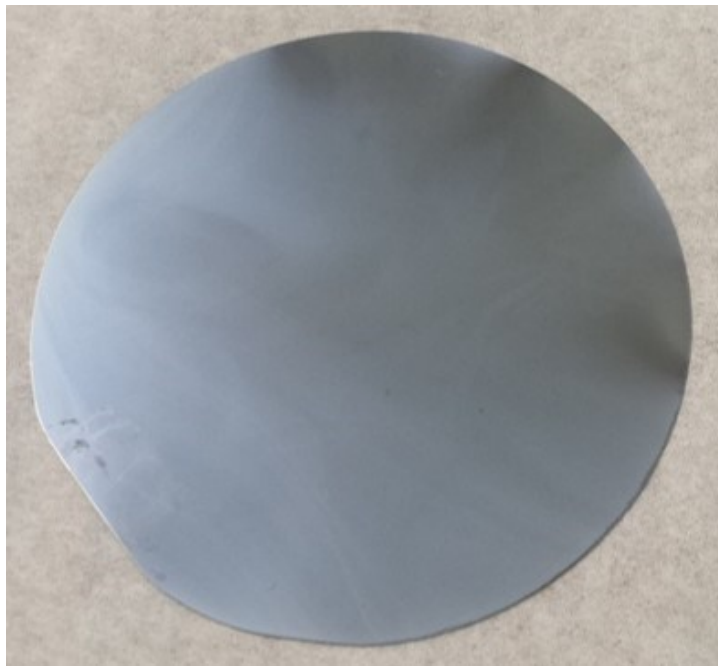


Figure 3.1 Picture of a sample with a rough surface. Surface roughness is apparent because the wafer is no longer mirror-like. In this figure it may be difficult to see the smoky appearance of the surface, as though some places are more mirror-like than other places.

still be playing a role. That being said, these observations do indicate that the gas molecules are receiving enough energy to react and form SiO_2 molecules. Based on these observations and the results of Watanabe et al., we conclude that a temperature of 900 °C is adequate for reliable deposition and smooth surfaces as long as the pressure is below 0.69 Torr. Keeping the pressure below this level allows for a longer mean-free-path and thus fewer collisions and less energy before reaching the substrate, where the heat from the substrate can finally provide the necessary energy for a reaction.

Another factor influencing the roughness of our films could be the rapid expansion of gas as it enters the deposition chamber resulting in condensation. According to Fukano [5], dichlorosilane delivery lines need to be heated in order to prevent condensation. However, heating the dichlorosilane delivery line to a temperature of about 100 °C did not eliminate roughness from our films. For example, refer to Table 3.1 where every sample listed was made with a heated dichlorosilane delivery line. Therefore, we conclude that while condensation needs considering when designing a low pressure CVD process, it is not the primary reason for the roughness of our thin films.

These theories and observations do not account for why placing more than one sample in the chamber at a time results in surface roughness while a single sample deposited under the same conditions is smooth. The conclusions we have made depend on pressure and energy as explanations for roughness, but neither pressure nor energy should be changed with the simple addition of substrates in the chamber. Further research is required to answer this question.

3.3 Comparison to Other Recipes

There are many recipes for silicon dioxide thin films using a variety of deposition or growth techniques. Table 3.2 lists some examples of recipes with various parameters and results. Different recipes are more or less useful for different applications based on the resultant properties as well

| Author | First Gas | Second Gas | Temp (°C) | Pressure (Torr) | Deposition rate (Å/min) |
|---------------------------|----------------------------------|------------------|--------------|--------------------|----------------------------|
| Klaus and George [2] | SiCl ₄ | H ₂ O | 20-26 | 0.6 - 3.6 | 0.1-16 |
| Watanabe et al. [4] | SiH ₂ Cl ₂ | N ₂ O | 900 | 0.6 | 55-70 |
| Chapple-Sokol et al. [3]* | SiH ₂ Cl ₂ | O ₂ | 450 - 675 | 760 | ≤ 1000 |
| McKeon and Allred | SiH ₂ Cl ₂ | N ₂ O | 900 | 0.65 | |

Table 3.2 Comparison of various CVD recipes for SiO₂. Note that every recipe uses different gases and thus require various parameters and yield different results. *Also note that the recipe used by Chapple-Sokol et al. incorporates a third gas (NH₃) as a catalyst.

as the actual parameters of the process itself. For example, scientist A may need to deposit silicon dioxide on a substrate that cannot withstand temperatures exceeding 500 °C, so she wouldn't want to use the same recipe that Watanabe used. However, if she is unable to put her sample in a vacuum chamber that can reach 0.6-3.6 Torr, she may not be able to use the same recipe as Klaus and George either. On the other hand, scientist B may not have any problem heating his substrate to temperatures exceeding 900 °C, and he wants to deposit at low pressures to avoid possible contaminants, so he could choose between those two recipes. Scientist B might choose the recipe that Watanabe used because it has a higher deposition rate, but if the silicon dioxide from that recipe has properties that he doesn't want he could choose another recipe altogether. For these reasons, it is important to carefully compare our results with other recipes.

Our recipe seems to agree fairly well with the work reported by Watanabe et al. [4]. Our work suggests that a slightly higher pressure than 0.6 Torr will result in smoother deposition without changing the deposition rate. However, we focused on varying pressure while Watanabe et al. held pressure constant and instead varied the ratio of dichlorosilane to nitrous oxide. It is possible that two or more distinct recipes could be identified within the range of gas ratios used by Watanabe and

the range of pressures we used. A more in-depth study with more accurate and reliable equipment would be needed to determine exactly how pressure and gas ratios effect the results of deposition.

3.4 Conclusions

From our experiment and analysis, we conclude that we can successfully deposit silicon dioxide thin films for a variety of applications, but that the specific parameters for optimal smoothness and uniformity lie within a narrow range and that there is little room for error. We verify that the parameters and methods used by Watanabe et al. [4] are satisfactory and result in reproducible and reliable deposition. However, we believe that recipe's parameters might be optimizable for smoother films.

From comparing the results of our experiment with the current literature, we observe that deposition of films from the reaction of silane with an oxidizing agent will in general occur at the same or lower temperatures as reactions of dichlorosilane with an oxidizer. Silane reactions also tend to have a larger range of pressures and temperatures in which successful deposition will occur when compared to dichlorosilane reactions. However, silane reactions also have slower deposition rates (see Table 3.2). Thus, where it is possible to exert greater control of temperature and pressure, a reaction involving dichlorosilane will often result in thicker layers faster than a reaction involving silane.

3.5 Directions for Further Work

Further work on this project should begin by exploring the range of pressures from 0.35 to 0.63 Torr. Once the effect of pressure on surface smoothness is mapped from low pressures resulting in no deposition to higher pressures that produce films just starting to become foggy, including quantitative data on the average roughness as a function of pressure, attention should be turned

to characterizing the boundary between homogeneous and heterogeneous nucleation. However, in order to get meaningful data in a reasonable amount of time, particularly with such small changes in pressure, I recommend first improving the equipment so that the parameters can be accurately controlled and time is not wasted on continuous repairs. With the current equipment, the pressure can only be controlled to a precision of about 0.1 Torr. The flow rates are much more accurate and can probably be controlled to about one sccm.

Once the effects of pressure, temperature, and gas ratios on the resulting deposition are understood, and a preferred recipe is decided upon, that recipe should be carefully characterized. Its deposition rate, as well as the resulting material's index of refraction, heat capacity, and other optical and physical properties should be studied and compared to silicon dioxide created in other ways.

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