
Science of Thin Films Activity

Deposition Overview for Microsystems

Participant Guide

Description and Estimated Time to Complete

Silicon dioxide (oxide) is a thin film used throughout microtechnology fabrication. Its applications include an insulating layer, a sacrificial layer, or a masking layer. A rainbow wafer is a wafer that is initially coated with a layer of silicon dioxide (SiO_2) or oxide (usually less than $6,000 \text{ \AA}$). This layer of oxide is then etched or removed in increments over a period of time (5 to 10 minutes). The result is the wafer you see here in the picture. Each layer, etched in equal time increments, appears to have a different color than the other layers. This is due to different thicknesses of oxide for each layer.



*Figure 1. "Rainbow Wafer"
[Courtesy of MJ Willis,
personal collection.]*

In this activity you learn why you see different colors for different thicknesses of oxide and the thickness of oxide that each color represents. Given a rainbow wafer, you estimate the thickness of several layers of silicon dioxide (SiO_2) based on the colors you see, then calculate the etch rate of each layer based on its thickness and time of etch. You also interpret graphs related to oxide growth and temperature.

This activity helps you to better understand the basics of oxidation and etch rate as they apply to the isotropic wet etch of silicon dioxide (SiO_2). It also helps you to begin to recognize oxide thickness based on its color and why the color changes with the oxide thickness.

Estimated Time to Complete

Allow at least 1 hour to complete this activity.

Activity Objectives and Outcomes

Activity Objectives

- Interpret Oxide thickness vs. temperature graphs.
- Using a color chart, estimate the thickness of silicon dioxide removed.
- Using your results, create two graphs showing the relationship between oxide thickness and time.

Activity Outcomes

By the end of this activity you should be able to estimate the thickness of a silicon dioxide layer by its color when viewing it from a specific angle and explain why the color of the oxide changes when viewed from different angles. You should also be able to calculate the time it would take to remove a specific amount of silicon dioxide under certain conditions.

NOTE: Part II – The Rainbow Wafer can be completed with the picture provided or you can order the SCME “Science of Thin Films Kit” which includes 2 processes “rainbow wafers”. This kit can be acquired through the SCME website (<http://scme-nm.org>) while supplies last and the center is funded.

Introduction

Silicon dioxide (SiO_2) is grown on a pure crystalline silicon wafer in a diffusion furnace using high temperatures (~ 900 to 1200°C). A diffusion furnace consists of a quartz tube large enough to hold several boats of wafers and able to heat to at least 1200°C . The wafers are placed in quartz boats. The boats are then placed on a platen (like a loading dock) which transports the boats into the furnace's quartz tube. Figure 2 shows the manual unloading of 100mm oxidized wafers.

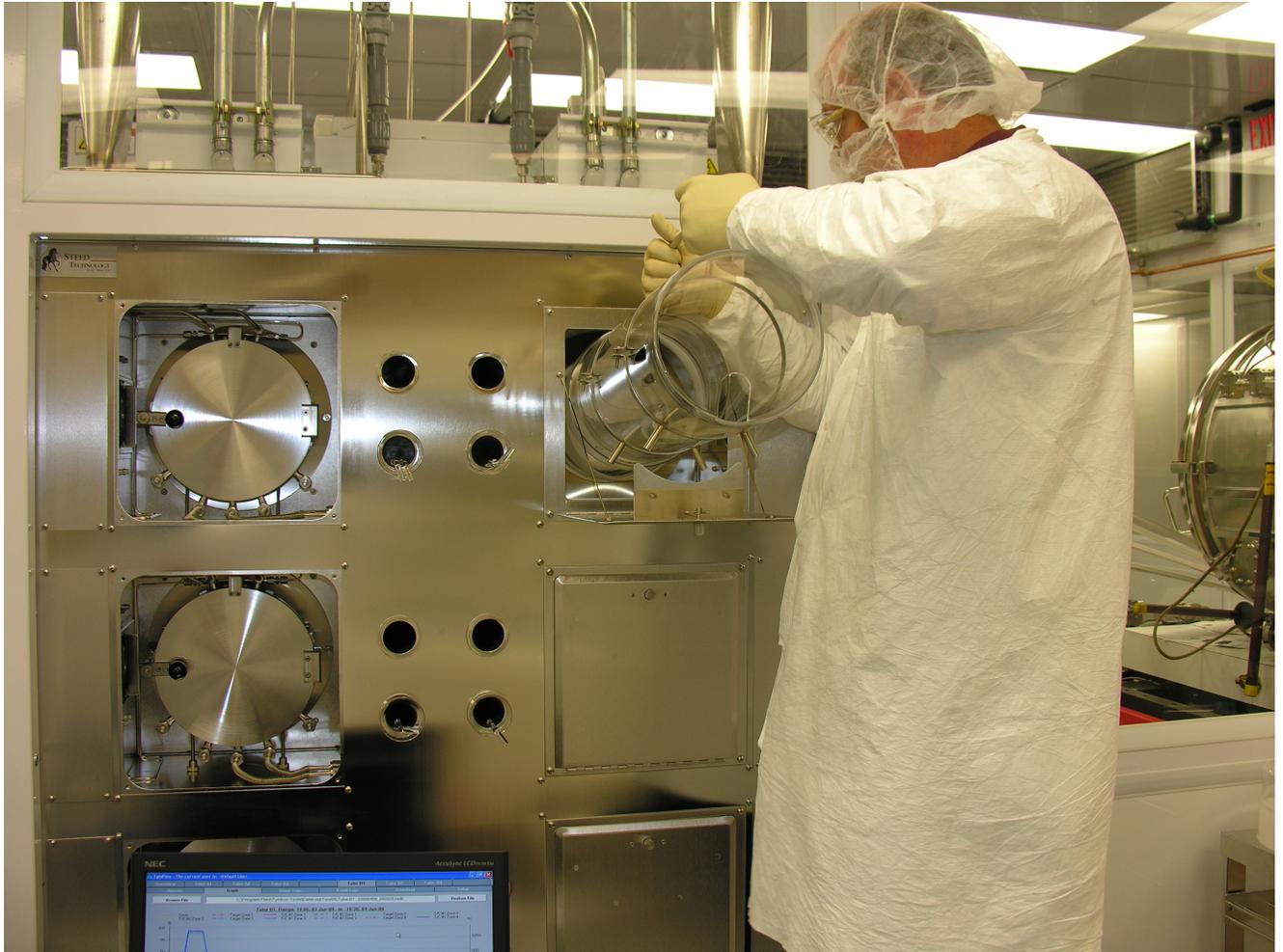


Figure 2. Oxidation furnace being manually unloaded.

[Image courtesy of the University of New Mexico, Manufacturing Training and Technology Center]

Growing Silicon Dioxide (Oxidation)

When exposed to oxygen, pure silicon (Si) oxidizes forming silicon dioxide (SiO₂). Silicon dioxide is also referred to as just “oxide” in the MEMS (microelectromechanical systems) industry. Additional names for silicon dioxide include “quartz” and “silica”. Native oxide is a very thin layer of SiO₂ (approximately 1.5 nm or 15 Å) that forms on the surface of a silicon wafer whenever the wafer is exposed to air under ambient conditions. This native oxide coating is a high-quality electrical insulator with high chemical stability making it very beneficial for microelectronics. Other benefits of SiO₂ in microelectronics and microsystems include the following:^{1,2}

- sacrificial layer or scaffold for microsystems devices
- structural layer or material for microsystems devices (beams, membranes)
- passivation coatings
- protect the silicon (“hard” mask)
- electrical isolation of semiconductor devices
- diffusion mask, a barrier material or mask during implant or diffusion processes
- gate dielectric and interlayer dielectric in multilevel metallization structures
- a key component in certain wafer bonding applications

SiO₂ naturally grows on a silicon surface at room temperature. However, this growth is very slow and stops at about 15 Å after only two to three days. In semiconductor and microsystems fabrication, SiO₂ is either deposited through a chemical vapor deposition (CVD) process or grown in a high temperature furnace with an oxygen source (gas or vapor). This latter process is called thermal oxidation.

The thermal oxidation process includes three basic steps (*Figure 3*):

- The silicon wafers are placed in a heated furnace tube (typically 900 – 1200 degrees C).
- A source of oxygen (gas or vapor) is pumped into the chamber. This source is either O₂ or H₂O, respectively.
- The oxygen molecules react with the silicon to form a silicon dioxide (SiO₂) layer in and on the substrate.

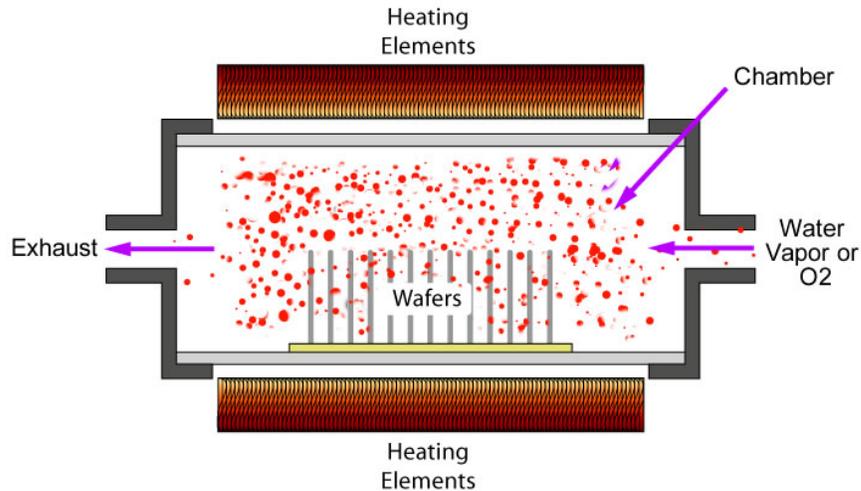
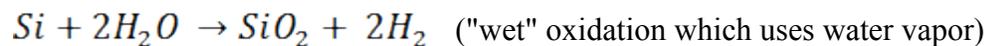


Figure 3. Schematic diagram of an oxidation furnace.

The chemical reactions that take place are



Oxide Growth Kinetics

This oxygen/silicon reaction is analogous to the oxidation or rusting of metal. In the case of iron (Fe), rust (Fe_2O_3) is formed. The rate of formation is dependent on the environment including the presence or absence of water (H_2O) and the temperature. The longer the metal or wafers are exposed to the oxygen source (H_2O or O_2), the thicker the rust (or oxide) layer becomes, to a point. The higher the temperature, the faster the reaction rate and the thicker the oxide. The oxide layer actually consumes a portion of the silicon just as rust consumes a portion of the metal.

Initially, the growth of silicon dioxide is a surface reaction only. However, after the SiO_2 begins to grow on the silicon surface, new arriving oxygen molecules must diffuse through the SiO_2 layer to get to silicon atoms below the surface. At this point the SiO_2 growth is occurring at the silicon crystal – silicon dioxide interface. As a general principle, the depth of pure silicon consumed in the oxidation process is 45% of the final oxide thickness (*Figure 4*). For every 1 micrometer of SiO_2 grown, about 0.46 micrometers of silicon is consumed.²

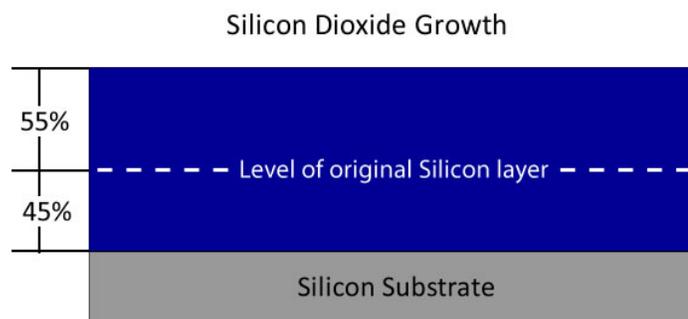
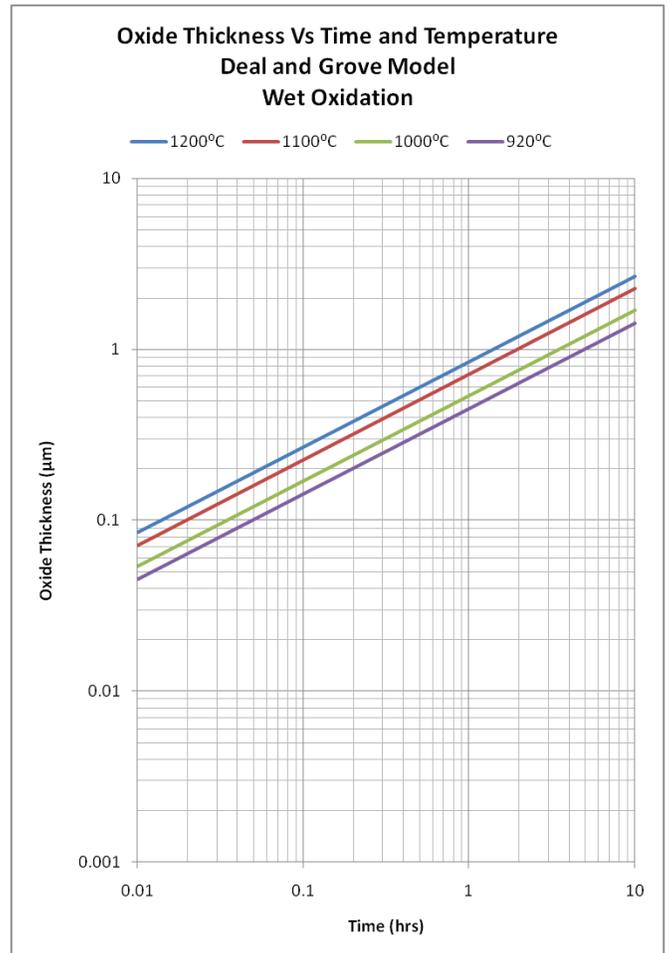
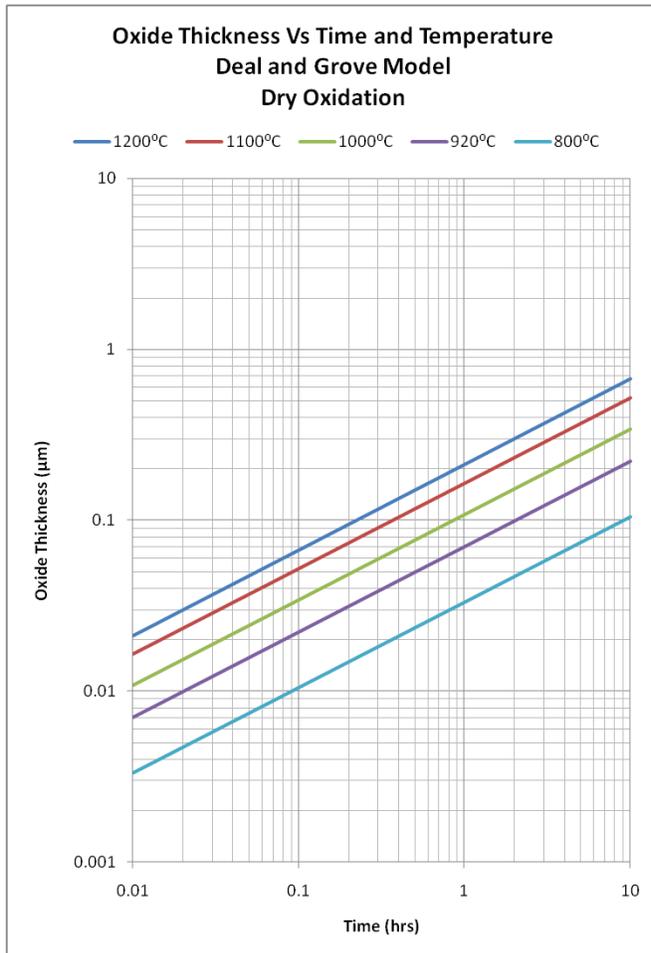


Figure 4. Cross-sectional view showing how silicon dioxide grows into the surface of the wafer surface.

The rate of oxide growth is highly dependent upon temperature. Let's take a look at the relationship between oxide thickness and temperature in dry and wet oxidation growth processes.

Activity Part I: Interpreting Oxide Growth vs. Temperature Graphs

Below are two graphs that demonstrate the growth rate of oxide relative to temperature in a dry oxidation process (*left graph*) and a wet oxidation process (*right graph*). These graphs closely match experimental data and are drawn based on a model by B.E. Deal and A. S. Grove.³



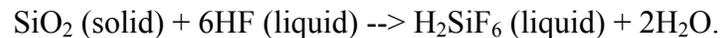
Answer each of the following based on your interpretation of the above graphs.

- In a wet oxidation process, how thick is the oxide after 1 hour when processed at 1200°C?
 - 0.1 μm
 - 0.2 μm
 - 0.9 μm
 - 2.0 μm
- In a dry oxidation process, how thick is the oxide after 1 hour when processed as 1200°C?
 - 0.1 μm
 - 0.2 μm
 - 1.0 μm
 - 2.0 μm

3. In a wet oxidation process of 1000°C, how long would it take to grow an oxide thickness of 1.0 μm?
 - a. 1 hour
 - b. 2.5 hours
 - c. 3.5 hours
 - d. More than 10 hours
4. In a dry oxidation process of 1000°C, how long would it take to grow an oxide thickness of 1.0 μm?
 - a. 0.1 hours
 - b. 1 hour
 - c. 4 hours
 - d. More than 10 hours
5. Based on your findings, which type of process yields a thicker oxide in a shorter period of time given the same temperatures?
 - a. Wet oxidation
 - b. Dry oxidation

Etching Silicon Dioxide

Silicon dioxide is readily etched using hydrofluoric acid (HF) according to the following reaction:



HF is a weak acid. This means that it only partially dissociates in water. Because of the low value of hydrogen ion concentration $[\text{H}^+]$ in weak acids (HF in our case), the pH is quite vulnerable to change. Changes in pH result in changes in etch rate. Small dilutions or consumption of the reactant during etching can significantly alter pH. These alterations can be limited by the technique of buffering the solution. The customary buffer for HF is ammonium fluoride (NH_4F). Ammonium fluoride is a salt that dissociates to form fluoride and ammonium ions. A typical volume ratio is 20 parts NH_4F to one part HF. This mixture is called buffered oxide etch (BOE). BOE is a reasonably selective etch for silicon dioxide. It will not etch bare silicon, but does attack silicon nitride and photoresist to some extent.

Oxide's Color

Oxide is colorless. However, when you look at an oxide wafer, it has color. The color of the oxide coated wafer is caused by the interference of light reflecting off the silicon (below the oxide) and the light reflecting off the top of the oxide surface. As the oxide thickness changes, so does the interference and the oxide's "seen" color. Color charts have been developed that state the oxide's thickness based on its "seen" color. (See the *Oxide Thickness Color Chart* attached.)

Figures 5, 6 and 7 illustrate thin film interference. When studying these figures, don't forget that white light consists of all of the colors of the visible light spectrum. You can see this when you shine white light through a prism (Figure 5).

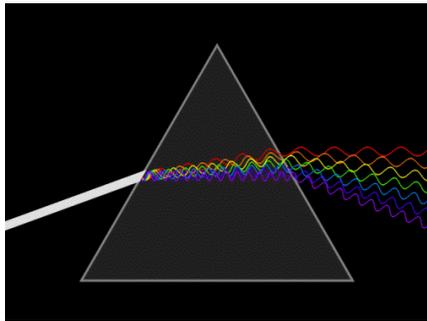


Figure 5. The dispersion of white light as it travels through a triangular prism. [Illustration is Public Domain]

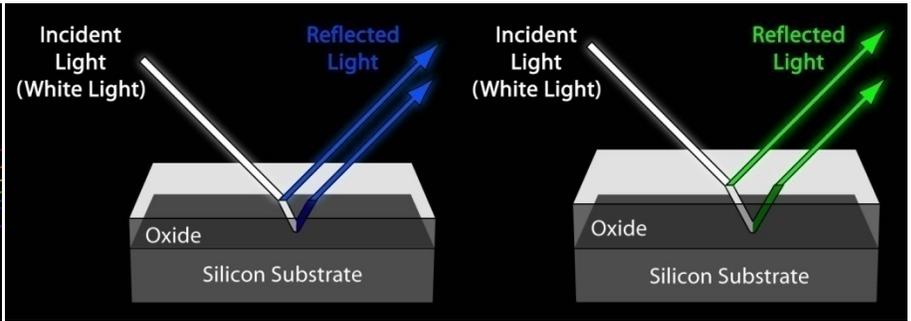


Figure 6. Two wafers with two different oxide thicknesses. The incident ray (or white light) is reflected off both the lower substrate/oxide interface surface and the top air/oxide surface. These two reflected rays of light recombine. Depending on the oxide thickness, only certain colors will constructively recombine, while the other colors which make up the white light will not. These two different thicknesses will reflect two different colors.

When the light reflected off the substrate is in phase with the light reflected off the surface of the oxide, the resultant wave is the sum of the amplitudes. This is *constructive interference*. If the two reflected waves are out of phase, then their amplitudes cancel each other out. This is *destructive interference*.

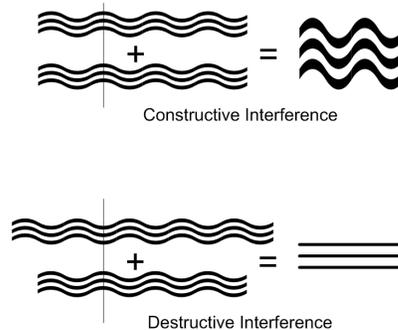
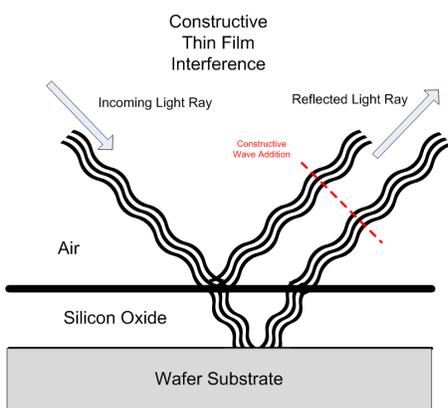


Figure 7. Constructive vs. Destructive Interference. The thin film interference effect is shown on the left for the case of constructive interference of a given wavelength of light and thickness of dioxide. The graphic on the right is a schematic representation of adding two waves which are in phase (constructive) and out of phase (destructive).

However, color can be deceiving. As you tilt the wafer, the color changes. In one wafer, of a specific thickness, you will see different colors as you view the wafer at different angles (tilt). The color you see depends on the angle at which you view the wafer's surface. Figure 8 is a series of photographs taken of the same oxidized wafers, but at three different angles (all of these wafers have had approximately 5700 Angstroms of oxide growth).

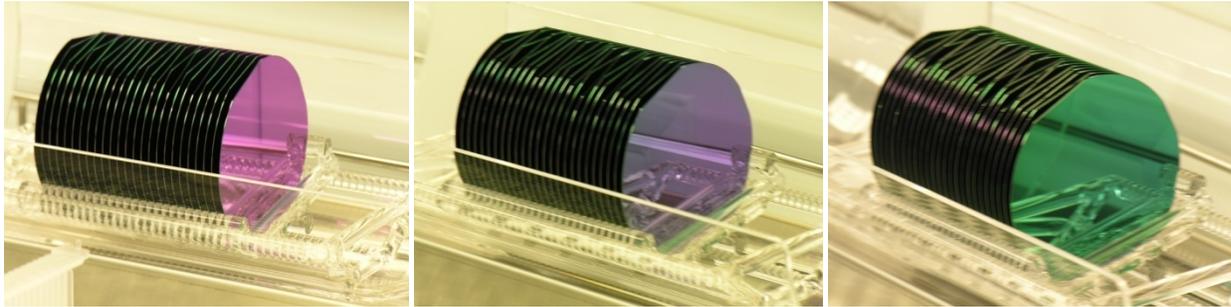


Figure 8. Three photographs taken of the same oxidized wafers at three different angles. [Photos courtesy of the University of New Mexico Manufacturing Training and Technology Center.]

The color you see comes down to the thickness of the film that the light travels through before reaching your eyes; this is called the optical path length. If you look straight down (perpendicular to the surface), the light reflected off the bottom (SiO_2 and Si) will have traveled through two times the thickness of the film. If you look at the same film at an angle, the light will have traveled through more than twice the thickness of the film; the light has therefore traveled through a longer optical path length. Effectively a thicker film is being observed; hence, the color looks different.

Therefore, to use a color chart to estimate oxide thickness consistently, it is very important that your line of sight is perpendicular to the wafer's surface. In other words, look straight down on the wafer, not at an angle.

Keep this in mind when completing this activity. Your outcome will be affected if you do not view the wafer from a direct, top-down perspective in a consistent manner.

Supplies / Equipment

- Rainbow wafer (provided in SCME Science of Thin Films Kit) and/or Rainbow wafer photograph (attached)
- Oxide thickness vs. Color Chart (Attached)
- Rainbow Wafer Calculations Worksheet (attached)

Documentation

- Activity Part I with answers
- Completed Rainbow Wafer Calculations Chart
- Required graphs with a written analysis for each graph
- Answers to the Post-Activity Questions

Activity Part II: The Rainbow Wafer

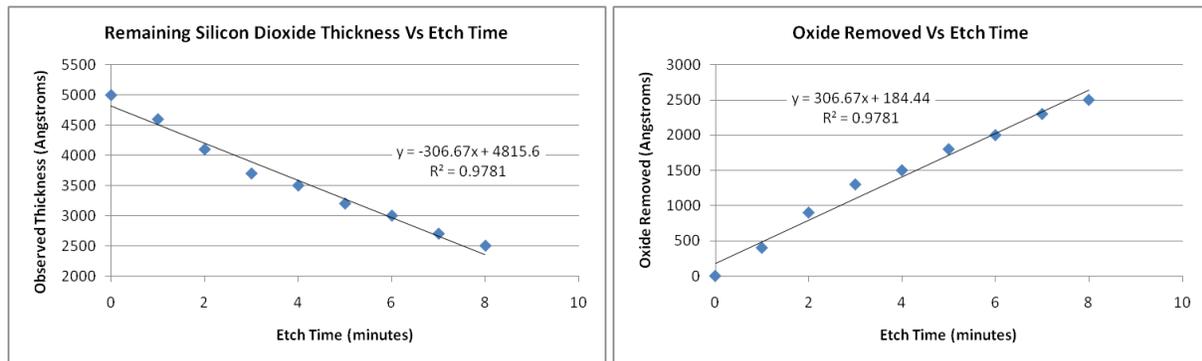
Description

Use a Rainbow Wafer and an Oxide Thickness vs. Color Chart to determine the oxide thickness of each color on the wafer. Develop several graphs from which you can extract the average etch rate. (The etch rate is the amount of oxide etched in a given amount of time.) The average etch rate can be determined by calculating the slope of the straight line through your data points.

Procedure:

1. Using the provided Rainbow Wafer or the Rainbow Wafer photo at the end of this activity, complete the Rainbow Wafer Calculations Worksheet.
 - a. **Determine the color of each stripe.** (Refer to Oxide Thickness vs. Color Chart)
 - b. **Determine the oxide thickness for each color** based on the color chart.
 - c. **Calculate the total amount of oxide etched (removed) for each stripe.**
 - d. NOTE: The rainbow wafer in the photograph has a starting oxide thickness of 5000 Å. If you are using the rainbow wafer from the activity kit, the starting oxide thickness will be noted in the kit.
2. **Using Excel or another spreadsheet software, plot a line graph** showing the relationship between "Remaining Oxide Thickness vs. Time Etched". Be sure to indicate units (Å, nm or μm).
3. **Plot a second line graph** showing "Etched Oxide (amount removed) vs. Time Etched". Be sure to indicate units (Å, nm or μm).
4. On each chart, **draw a trend line through your data points.** (If you're using Excel, right click on a point on your chart, select "Add Trend line", then select "linear". If the software doesn't have the capability to add a Trend line, you'll need to estimate it. Draw a straight line through your points that "best fits" the trend of the data points.
5. **Select two points on the line** (points that are NOT your data points) where the line crosses an axis.
6. Use the two points to **determine the slope of the line.**
7. **Answer the Post-Activity Questions.**

Examples of plotted data



Oxide thickness Vs Etch time on the left graph. Oxide thickness removed on the right graph. Both graphs include the fitted straight line trend and corresponding equations with the goodness of fit, R (when $R=1$, the fit is perfect). The equation follows the $y = mx+b$ equation of a straight line where m is the slope of the line.

Post-Activity Questions

1. What does the slope of the line (m) represent?
2. Refer to your graph for "Remaining Silicon Dioxide Thickness vs. Etch Time".
 - a. What is the slope of this line-graph? What is the equation of the line? Make sure you include the units.
 - b. The slope should be negative. What does a negative slope mean in this context?
3. Refer to your graph for "Oxide Removed vs. Etch Time".
 - a. What is the slope of this line-graph? What is the equation of the line? Make sure you include the units.
 - b. The slope should be positive. What does this mean?
 - c. How does this compare to question 3) above?
4. Based on your graphs and the slope of the line, how long does it take to etch 0.05 microns (μm) of oxide?
5. Given a silicon wafer substrate with 500 nm layer of oxide, how long would it take to etch to bare silicon based on your data?
6. Refer to the Oxide Thickness vs. Color Chart. What is the thickness(es) of a wafer that looks "yellow-green"? (You may see "yellow-green" more than once. Include all thicknesses.)
7. Why do oxide colors repeat as the oxide continues to grow?

8. In a fabrication facility, estimating the oxide's thickness based on its color is used as an initial verification by the operator that the oxidation process was correct. However, it is not accurate. How is oxide thickness measured in a fabrication facility?
9. Refer to your actual data points. What factors contribute to the variations between data points? (Theoretically, the data points should line up in a straight line with a constant etch rate.)
10. List three other types of thin films used in microtechnology and describe the purpose or applications of each of these thin films.

Summary

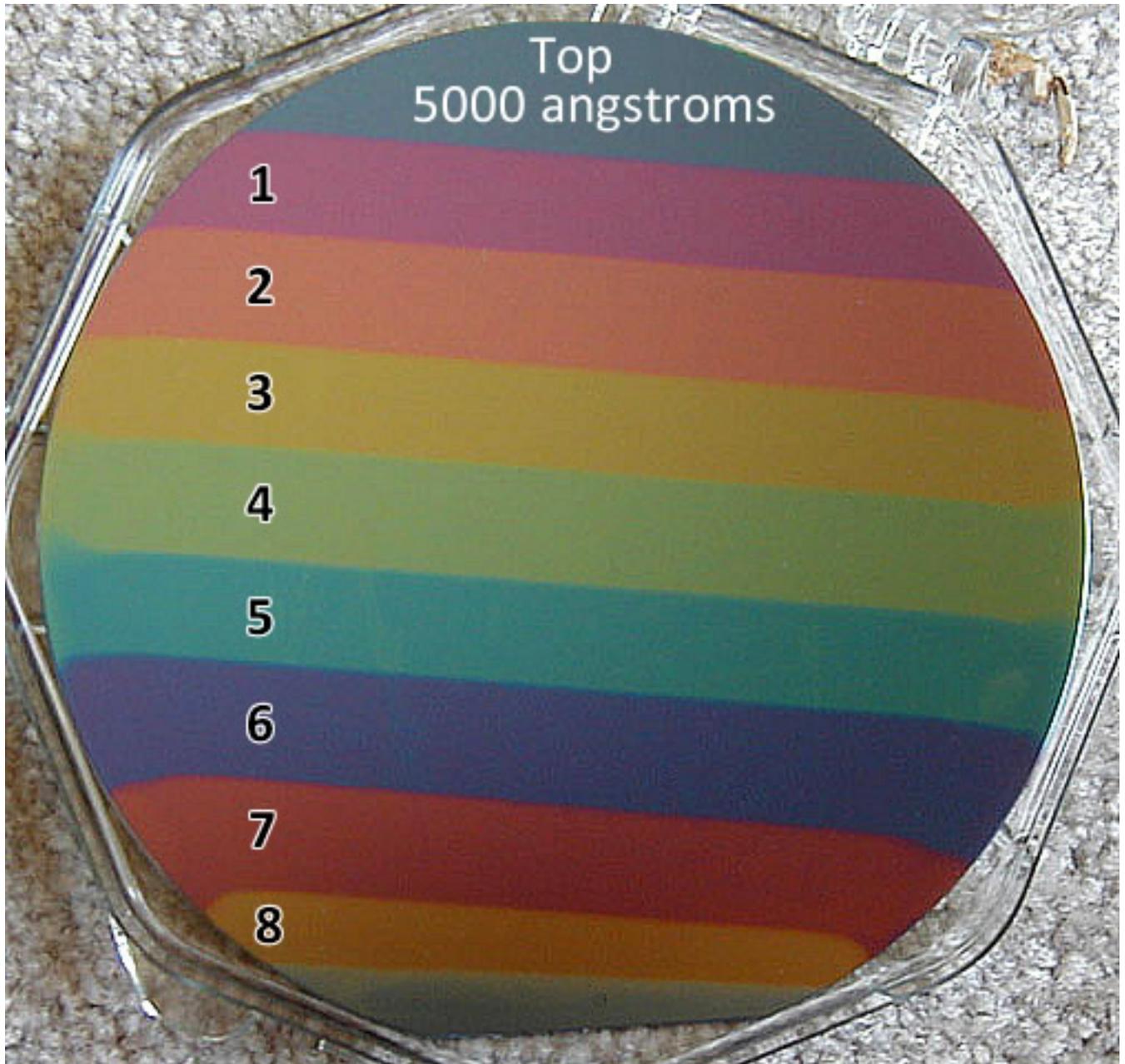
When exposed to oxygen, silicon oxidizes forming silicon dioxide (SiO_2). Thermal oxidation is used to grow precise thicknesses of oxide on bare silicon wafers. Even though oxide is transparent, the interference of white light reflected off the silicon crystal/oxide interface with that reflected off the oxide's top surface, creates a variation in color depending on the thickness of the oxide.

Hydrofluoric Acid (HF) can be used to etch SiO_2 . The longer the etch time, the more oxide is removed. If you know the etch rate and the initial oxide thickness, you can calculate the amount of time needed to remove a specific thickness of oxide or how long you need to etch an oxide coated wafer to get a specific thickness.

References

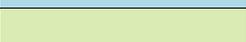
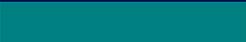
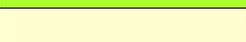
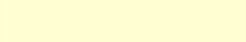
1. "General Relationship for the Thermal Oxidation of Silicon" B. E. Deal and A. S. Grove, Journal of Applied Physics, Vol. 36, No. 12 (1965).
2. "Photolithography (Oxide Etching) Lab". Albuquerque TVI. Mary Jane Willis and Eric Krosche. (1996)
3. "Oxide Growth and Etch Rates". MEMS 1001. Central New Mexico Community College. Matthias Pleil. (2008).

Support for this work was provided by the National Science Foundation's Advanced Technological Education (ATE) Program through Grants. For more learning modules related to microtechnology, visit the SCME website (<http://scme-nm.org>).



This Rainbow Wafer was created by lowering the wafer into BOE one stripe at a time. Each interval was held (by an operator) for 1 minute, then lowered to the next level. This wafer was created in approximately 9 minutes. The bottom most level was in the BOE solution for the entire 9 minutes. The top most level (5000 angstroms) was never exposed to the BOE.

Oxide Thickness vs. Color Chart

Oxide Thickness [Å]	COLOR	Color and Comments
500		Tan
750		Brown
1000		Dark Violet to red violet
1250		Royal blue
1500		Light blue to metallic blue
1750		Metallic to very light yellow-green
2000		Light gold or yellow slightly metallic
2250		Gold with slight yellow-orange
2500		Orange to Melon
2750		Red-Violet
3000		Blue to violet-blue
3100		Blue
3250		Blue to blue-green
3450		Light green
3500		Green to yellow-green
3650		Yellow-green
3750		Green-yellow
3900		Yellow.
4120		Light orange
4260		Carnation pink
4430		Violet-red
4650		Red-violet
4760		Violet
4800		Blue Violet
4930		Blue
5020		Blue-green
5200		Green (Broad)
5400		Yellow-green
5600		Green-yellow
5740		Yellow to Yellowish (May appear to be light creamy gray or metallic)
5850		Light orange or yellow to pink borderline
6000		Carnation pink

Rainbow Wafer Photo Calculations Worksheet
(Use for Rainbow Wafer Photo)

Level	Color	Oxide Thickness*	Total Etch Time	Å Etched (Starting Oxide – Oxide Thickness)
Pre-Etch	Bluish Green	5000 Å = 500 nm	0 seconds	0 Å
1			1 minute	
2			2 minutes	
3			3 minutes	
4			4 minutes	
5			5 minutes	
6			6 minutes	
7			7 minutes	
8			8 minutes	

*The values in the answer key are “measured values”. Participants will be using “estimated values” based on the color chart.

Rainbow Wafer Calculations Worksheet (Use for Rainbow Wafer in kit)				
Level	Color*	Oxide Thickness*	Total Etch Time	Å Etched (Starting Oxide – Oxide Thickness)
Pre-Etch	Green	5200	0 seconds	0 Å
1			25 seconds	
2			50seconds	
3			75seconds	
4			100seconds	
5			125seconds	

*The values in the answer key are “measured values”. Participants will be using “estimated values” based on the color chart.