JOURNAL OF
EMERGING INVESTIGATORS

Article

Converting SiO_2 wafers to hydrophobic using chlorotrimethylsilane

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SUMMARY

Semiconductors are the center of the fourth industrial revolution as they are key components for all electronics. To manufacture chips, semiconductor companies purchase bare wafers and perform many different processes to ensure the finest quality of each chip. Exposed wafers made of silicon (Si), which can easily oxidize, convert to silicon dioxide (SiO_2). The surface of SiO_2 wafers consists of many Si-OH bonds, allowing them to easily bond with water, resulting in a "wet" or hydrophilic condition. The hydrophilic condition of a wafer can be problematic as the fin can collapse during water rinsing. We sought to determine a way to modify the surface of SiO_2 wafers to become hydrophobic to ensure safe wet cleaning. We hypothesized that treating the surface of the wafer with hydrophobic chemicals like chlorotrimethylsilane (CTS) could address this problem by converting the surface of the wafer into Si-OR (R group being hydrocarbons). This conversion would prevent hydrogen bonds from forming with water, which would then convert the wafer from hydrophilic to hydrophobic. After executing the experiment, the hydrophobicity was analyzed by measuring the contact angle of the wafer, where increases in contact angle portrayed a more hydrophobic surface. In our results, there was an increase in contact angle, which concluded that coating the SiO_2 wafer with CTS repels water from the surface, therefore allowing for a safe cleansing process. The prevalence of semiconductors today makes it especially important for maximum efficiency in the industry; a rinsing process minimizing risks would curtail costs and time.

INTRODUCTION

Currently, the world is experiencing a fast-changing process known as the fourth industrial revolution, with semiconductors at its center (1). Semiconductors are essential as they can be used in many industries such as computing, healthcare, military systems, and transportation. The 4th Industrial Revolution is possible due to a miniscule chip known as the integrated circuit (IC), and in 2022, the market for integrated circuits was around 350 billion to 560 billion US dollars (2). The IC, around 2 mm by 2 mm, consists of electronic components, such as transistors, diodes, resistors, and capacitors, that must function together precisely to perform logic operations and store data (3). Without ICs, modern society would not be able to maintain its current status due to highly computerized systems. The wafer is the base of the IC on which it is built and through which electricity flows. The purpose of this research was to discover and experiment with ways to prevent issues with the wet cleaning process of ICs.

Although germanium wafers are occasionally used, silicon-based wafers are more popular. Firstly, silicon is one of the most abundant elements on earth, making it easily accessible. In addition, silicon wafers have a high heat resistance of about 150°C, while germanium wafers can break down at temperatures as low as 70°C (3).

To manufacture the finest quality ICs, semiconductor companies must perform six critical main steps: deposition, photoresist coating, etching, ionization, lithography, and packaging (4). However, these steps are not the complete picture of semiconductor processes of making ICs (5,6). Along with the six main steps, there are other sub-steps, such as electroplating, wafer testing, and cleansing, which a wafer must go through hundreds of times before becoming a part of a device (5,7). During the cleansing step of a wafer, a specific method, wet cleaning, is generally preferred because it uses non-toxic chemicals, such as water. However, wet cleaning can still damage wafers, from silicon (Si) oxidation

https://doi.org/10.59720/23-100

through water droplets, residue of silica eluted from water, particle adhesion due to electrostatics, and water residue (8). These result in downstream process failure, enlarged thermal capacity of the wafer, and gate structures collapsing during the drying step (9). These issues can arise from every wet cleaning step and result in degraded IC performance. To minimize the chance of these issues, many techniques, such as optimizing the amount of water used, using precise cleaning times, increasing drying time, and changing distilled water to ultrapure water, can be used. However, the issues with reduced performance cannot be avoided completely (8).

Thus, in this study, we sought to remedy some of the current issues with wet cleaning of wafers and issues with fin collapse. We hypothesized that changing the surface of the wafer from hydrophilic to hydrophobic would repel water because it would be unable to hydrogen bond with the surface of the wafer. If the exposed wafer is mostly made of SiO_2, then the surface of the wafer will contain many Si-OH bonds, thus resulting in a hydrophilic property. However, if the Si-OH surface is converted to Si-OR, water will repel the surface of the wafer due to the intermolecular forces at play. Repelling the water provides a hydrophobic contact angle, a larger angle between the surface of the wafer and the water droplet (**Figure 1**). We can convert Si-OH to Si-OR through a Substitution 2 (S_N2) reaction. In this type of reaction, a nucleophile attacks an alkyl halide (10). In our experiments, the oxygen from Si-OH acted as a nucleophile and knocked out chlorine (Cl) from chlorotrimethylsilane (CTS) to yield Si-OR.

To start the research process, we hypothesized that using chemicals like CTS would be able to make the hydrophilic Si-O_2 wafer into a hydrophobic one. We decided to use CTS as it can easily undergo S_N2 reactions with Si-OH. Additionally, although there are various alkyl halides, such as bromotrimethysilane and iodotrimethylsilane that can also undergo S_N2 reactions with Si-OH, the byproducts can be extremely corrosive and toxic, which is why we chose only CTS as the reagent (11). After the successful conversion of Si-OH bonds on the surface of the wafer into Si-OR through the S_N2 reaction, we used a goniometer (Ossila) to calculate the contact angle to measure the hydrophobicity of the wafer. Afterwards, if the reaction did not proceed fast enough, we would force the reaction by heating the wafer using temperature controllable hotplates (FOUR E's scientific hot plate), therefore optimizing the process. Through the experiment, we found that the CTS was able to convert the surface of the wafer to have hydrophobic properties, which allows for a safer, more efficient method for the wet-cleaning process of silicon wafers.

Figure 1: Explaining Contact Angle. The contact angle of a water droplet is the angle of the bottom curve to the surface of the wafer. In this figure, the contact angle is very high, suggesting that the surface is hydrophobic because it is repelling the water.

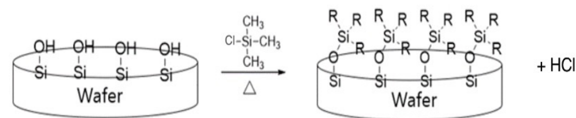

Figure 2: Reaction mechanism of chlorotrimethylsilane (CTS) on the surface of a SiO_2 wafer. This figure shows how CTS bonds to the surface of SiO_2 via an S_N2 reaction, releasing HCl as a byproduct.

RESULTS

To test our hypothesis, we sought to convert Si-OH on the surface of the wafer to Si-O-SiR_3. We placed the wafer on a hotplate for 10 minutes before carrying out experiments of coating the wafer with CTS. We rinsed the wafer with 10 mL of DI water and 5 mL of 100% acetone before and after every experiment. Then, the wafer was air-dried through a compressed air duster (air speed ~43m/s) to remove any remaining residues such as water, acetone, or silicon-based oil. Throughout the experiment, we optimized conditions by adjusting the temperature, amount of CTS, and reaction time.

While carrying out the reaction, there was one serious caution that needed to be taken. According to our mechanism (**Figure 2**), acid will form when Si-OH reacts with Si-Cl, creating hydrochloric (HCl) acid. HCl, a corrosive acid, will convert the Si-O-SiR_3 bond back to Si-OH due to the reverse S_N2 reaction if water was present in the reaction. For this reason, rather than capturing the water molecule to stop the reverse S_N2 reaction, we added small amounts of a base, triethylamine, to neutralize the acid byproduct.

To analyze the data, we measured the contact angles of droplets of water on the surface of the wafer using a goniometer. In our research, we considered that if the contact angle was low, then the hydrogen bonds would bind water to the surface of the wafer and therefore damage the surface tension. Conversely, if the hydrogen bonds were not able to bind water fully, it would lead to a higher contact angle (**Figures 1 and 3**). Ultimately, this means that a relatively lower contact angle would represent a more hydrophilic surface compared to a water droplet with a higher contact angle, which would be more hydrophobic. We took the reference data without treating the SiO_2 wafer with CTS, and all our data was collected as an average (the average contact angle referring to the average of the different results from using multiple drops of CTS on the same wafer). The reference showed that the surface of the SiO_2 was hydrophilic due to the low average contact angle.

After taking the reference data, we tested the wafers in different conditions. Firstly, to optimize the reaction time, the

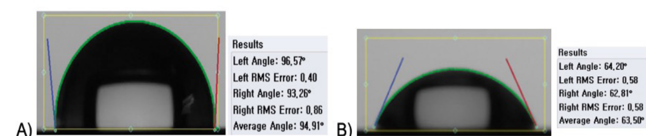

Figure 3: Contact angle analysis. After the wafers were treated with CTS to convert the hydrophilic surface to a hydrophobic one, the contact angle was measured using a goniometer. A) The contact angle for a water droplet on a CTS treated SiO_2 wafer. Panel A has a lower contact angle (left angle: 64.20° and right angle: 62.82°) due to a hydrophilic surface and B has a higher contact angle (left angle: 96.57° and right angle 93.26°) due to a hydrophobic surface. B) The reference with a water droplet on untreated SiO_2 wafer.

https://doi.org/10.59720/23-100

Experiment	Amount of CTS (mL)	Temperature (C°)	Reaction Time (s)	Average Contact Angle (°)
1	0.5	85	1	74.24
2	0.5	85	3	81.11
3	0.5	85	5	90.55
4	0.5	85	7	89.93

Table 1: Contact angle results depend on the reaction time. The table below suggests that the most optimal reaction time was 5 seconds. Less than 5 resulted in a lower contact angle as did longer reaction times.

time CTS was left on the surface was set to 5 seconds, as the CTS would evaporate quickly at high temperatures if left any longer (**Table 1**). At 5 seconds, the water droplet was at an optimized contact angle at 90.55° (most hydrophobic). Any more or less time and the angle decreased. Then, we optimized the temperature to 85°C because at higher temperatures, the CTS would evaporate quickly, and at lower temperatures, the contact angle would not be optimal (**Table 2**). Examining the trendline of the contact angle in regards to temperature, we noticed that the angles overall increased, and peaked at 85°C (**Figure 4**). Afterwards, we optimized the amount of CTS used at 0.1 mL (**Table 3**).

The contact angle after treating the surface of the SiO_2 wafer with CTS increased at 85°C (**Figure 3A**) compared to other temperatures such as 25°C, which was not treated with the chemical (**Figure 3B**). In addition, the data of the various contact angles based on the amount of chemical that was used (**Table 2**). We used the same method and cleaning as the previous conditions. As the amount of CTS increased, the average contact angle did not continue to significantly increase. Using more than 0.1 mL of CTS decreased the contact angle, leading to the conclusion that the most optimal amount was 0.1 mL of chemical. We used the data above to create the most optimal results by increasing the contact angle from a non-treated wafer with 0.1 mL of CTS and an increased temperature of 85°C.

DISCUSSION

We performed experiments to test if CTS would effectively block water from interacting with the wafer during wet rinse. The first reaction that was conducted was changing the length of reaction times. When looking at the data, we concluded that any time less than 5 seconds was not providing enough time for the reaction to fully coat the wafer. However, any time longer than 5 seconds seemed to not provide a noticeable change. This result led us to believe that time longer than 5 seconds did not provide an important enough change to leave the reaction to run for longer.

Experiment	Amount of CTS (mL)	Temperature (C°)	Reaction time (s)	Average Contact Angle (°)
Reference	-	25	-	63.50
1	0.1	45	5	80.11
2	0.1	55	5	87.04
3	0.1	65	5	88.60
4	0.1	75	5	89.64
5	0.1	85	5	94.80
6	0.1	95	5	93.37

Table 2: Contact angle results depend on the reaction temperature. Contact angle increases as the reaction temperature increases due to faster reaction of CTS on the surface of SiO_2 wafer. The maximum average contact angle was achieved at 85°C.

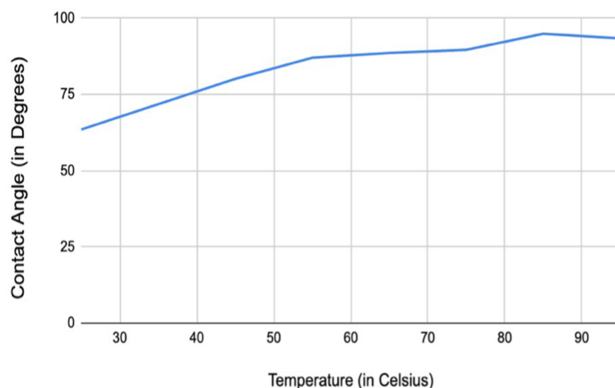

Figure 4: Trendline of Contact angle vs. Temperature (°C). The trendline shows that the higher the temperature, there was typically a higher contact angle (which is desired).

Afterwards, we changed the temperatures of the wafers. We found that the most optimal temperature was 85°C. Although CTS reacted to form a hydrophobic surface at lower temperatures such as 45°C, we found that the reaction would occur at a higher temperature. However, going over 85°C provided similar or worse results because the CTS would evaporate due to its low boiling point. In the case of the wafers tested, we found that using more than 0.1 mL of CTS was unnecessary as there was an excess amount of the chemical, providing similar results to using more CTS. Using less than 0.1 mL was less effective as the wafer did not seem to become fully coated. Using our results, we concluded that the CTS chemical at 85°C with 0.1 mL was the most efficient in creating a hydrophobic wafer. Our research reveals an important step forward towards the possibility of making the wet-cleaning process more efficient and safer at a low cost in the semiconductor industry.

There are a few things we can do to further expand this project. Although our experiment with CTS provides a substantial amount of change already, it could potentially be more effective if we could find a larger, more nonpolar molecule like tert-butyldimethylchlorosilane to treat the wafers with to block additional water and take advantage of steric hinderance, the ability to slow chemical reactions with steric bulk. We believe bigger molecules can potentially repel more water because of their larger surface area. This avenue of research can be beneficial; if more water is repelled, the more potential there is in semiconductor production efficiency. We could do also identify a molecule that does not give off unwanted byproducts like the hydrochloric acid that CTS produces.

Experiment	Amount of CTS (mL)	Temperature (C°)	Reaction time (s)	Average Contact Angle (°)
1	0.01	85	5	78.32
2	0.03	85	5	82.11
3	0.05	85	5	85.89
4	0.07	85	5	88.22
5	0.1	85	5	94.80
6	0.2	85	5	90.54

Table 3: Contact angle results depend on the amount of CTS. Average contact angle increases when more CTS is used. Maximum average contact angle was obtained by using 0.1 mL of CTS

https://doi.org/10.59720/23-100

MATERIALS AND METHODS

To start, we made sure that all of our experiments were conducted in a "neat" condition, which is when there are no solvents. To make the experiment "neat", we conducted experiments with a small amount of triethylamine to quench any acid byproduct. For our reference angle, after it reached the temperature we wanted, we put 0.1 mL of water onto the surface of the wafer which was then placed on top of the goniometer. The goniometer measured the contact angle which we analyzed. We repeated this three times and averaged to find the average contact angle.

To optimize our reaction time, the hot plate temperature was adjusted to a predetermined target temperature of 85°C. Once the temperature was reached, we waited 10 minutes to minimize the fluctuation of the target temperature. The silica wafer was placed on the hot plate, and we waited another 10 minutes. After reaching the target temperature, 0.1 mL of 99.3% pure chlorotrimethylsilane was injected onto the surface of the wafer within 10 seconds. The wafer was removed from the hot plate after different increments of time and rinsed with 10 mL of distilled water and 5 mL of acetone and then air-dried using a compressed air duster. The different times that were tested were 1, 3, 5, and 7 seconds. The surface treated wafer was placed on the goniometer and the contact angle was measured the same way the reference angle was measured (with the water droplet).

Afterwards, we optimized the temperature. We adjusted the hot plate temperature to 25, 45, 55, 65, 75, 85, and 95°C. The following steps for coating the wafer were the same as above, with the time fixed at 5 seconds. The hydrophobicity of the surface was then tested using the water droplet and the goniometer.

Finally, the volume/amount of CTS was optimized. The hot plate was heated to 85°C. When coating the wafer this time, we fluctuated the amounts of CTS instead of adjusting the time or the temperature. We used 0.01, 0.03, 0.05, 0.07, 0.1, and 0.2 mL of CTS in our experiments. The CTS was left for 5 seconds before rinsing and measured for contact angle.

ACKNOWLEDGMENTS

We would like to thank Professor Isaac Edminster at George Fox University for his contribution to proof-reading and correcting the paper. Furthermore, we would like to thank Professor Hongjae Cho at Oklahoma University for his guidance and ideas on carrying out experiments safely.

Received: November 15, 2022
Accepted: November 7, 2023
Published: August 20, 2024

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