**Hydrogen peroxide to strong base ratio of 1:1 prevents silicon from etching during RCA clean**

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RCA cleans are among the most common procedures performed in the SMFL at RIT. The purpose of such cleans is to effectively remove organics, heavy metals, and inorganic residues. Although the exact chemical composition of RCA cleans vary among laboratories, they generally consist of three main components: a Standard Clean 1 bath (SC1), a Hydrofluoric Acid (HF) dip, and a Standard Clean II bath (SC2). The SC1 contains a strong base, normally ammonium hydroxide, and hydrogen peroxide and the SC2 contains a strong acid, normally hydrochloric acid, and hydrogen peroxide. The purpose of hydrogen peroxide in the RCA clean is to react with the exposed silicon surface of the wafer to form a chemically grown oxide, protecting the wafer from being etched in the strong base or acid. Because the hydrogen peroxide reacts directly with the silicon on a wafer, the amount needed depends both on the amount of silicon exposed on the wafers and the number of silicon wafers being cleaned.

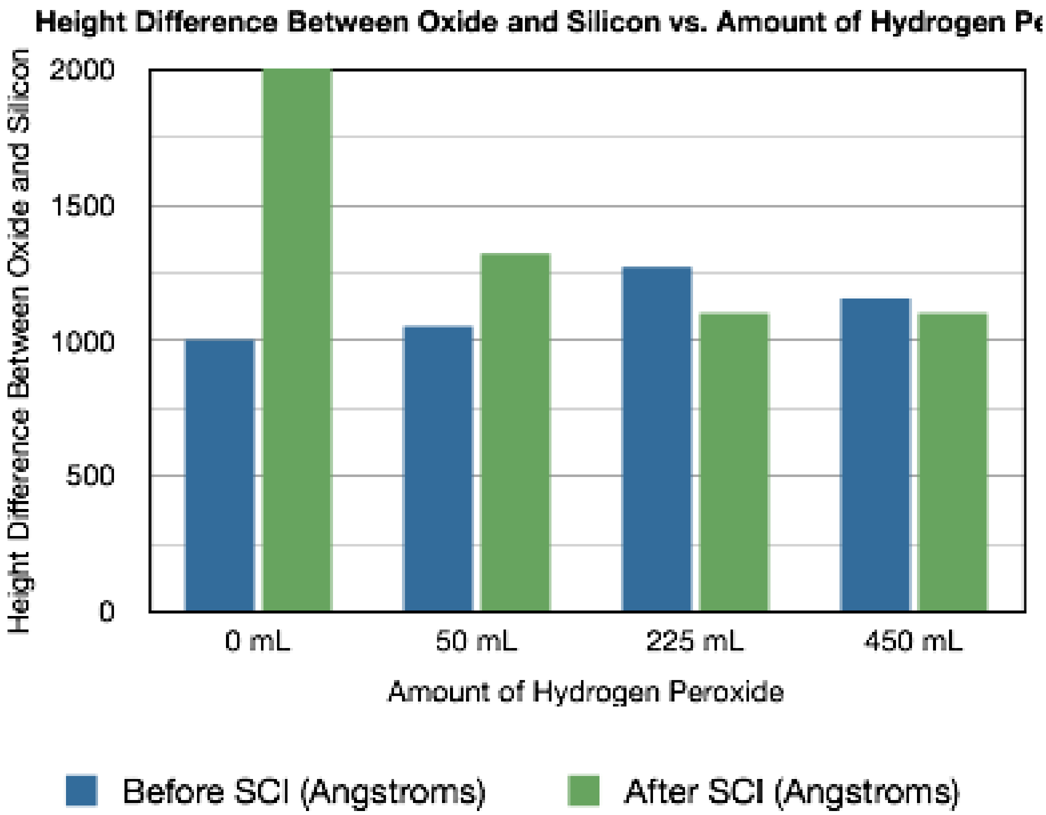
RIT currently uses a 15:3:1 ratio of water, hydrogen peroxide, and ammonium hydroxide or hydrochloric acid respectively. This is equivalent to 900 mL of hydrogen peroxide per bath and 1,800 mL per RCA clean, amounting to $9.30 spent for each clean on hydrogen peroxide. The quantity of hydrogen peroxide per RCA clean used by RIT is three times the amount used by other top university FABs, which unanimously use a 1:1 ratio of hydrogen peroxide to acid or base. Adopting this standard 1:1 ratio for RCA cleans as used in the industry could save RIT as much as $2,500 per year.

Six inch silicon wafers can be patterned and submerged in SC1 and SC2 baths with varied amounts of hydrogen peroxide. The amount of etching, or lack thereof, can be measured using the Tencore P2 Profilometer, which measures the height between silicon and oxide before and after the clean. Once a ratio is found that does not change the height measurement before and after the RCA clean, it was used for all RCA cleans in RITs Metal Gate PMOS process. The transistors on the wafers were then tested to verify that the device characteristics were not changed.

We used this method to test how much hydrogen peroxide is needed to protect a silicon wafer in SC1 and SC2. The amount of silicon etching was observed and measured. The amount of chemically grown oxide needed to protect the wafer was also measured, as was the etch rate of the 50:1 HF. We report here on a 1:1 ratio of hydrogen peroxide to strong base that effectively protects a silicon wafer from being etched in SC1. It was also determined that the length of time wafers spend in the 50:1 HF dip can be reduced by at least half, making the dip 30 seconds. This helps retain wanted oxide thicknesses such as the gate oxide in the metal gate process. Finally, we determined that the hydrochloric acid in SC2 does not etch silicon. We present data that provides evidence that the RCA clean should be changed such that: the amount of hydrogen peroxide needed in SC1 and SC2 is one third of the currently used amount.

## Results

In order to determine the amount of hydrogen peroxide that must be added to SC1 to prevent silicon etching, 4 six-inch silicon wafers with 1,000 angstroms of oxide were coated, exposed, developed and etched. Following this the photoresist was removed leaving a patterned oxide wafer. The back of the wafer was bare and the front was mostly bare with some small oxide features. The Tencore P2 Profilometer was used to measure the height difference between the oxide and exposed silicon in a specific location at the center of the wafer. Next, wafers were submerged in baths for 15 minutes at 75 degrees Celsius containing 300 mL ammonium hydroxide, water, and either 0 mL, 50 mL, 225 mL, or 450 mL hydrogen peroxide. The height difference between oxide and silicon was then again measured with the Tencore P2 Profilometer in the same previously measured location. As seen in Figure 1, when SC1 had no added hydrogen peroxide, the height difference between silicon and oxide increased from 1,005 angstroms to 70,900 angstroms. When SC1 had only 50 mL of hydrogen peroxide, the height increased from 1,054 angstroms to 1,323 angstroms before and after submersion in the bath (Figure 1). If 225 mL of hydrogen peroxide was added to SC1, the height difference between oxide and silicon decreased from 1,274 angstroms to 1,103 angstroms (Figure 1). Finally, when 450 mL of hydrogen peroxide were added to SC1, the height difference between oxide and silicon decreased from 1,158 angstroms to 1,103 angstroms (Figure 1). A decrease indicates no etching and growth of a chemically grown oxide.




| Amount of Hydrogen Peroxide (mL) | Before SC1(Angstroms) | After SC1(Angstroms) |
|---|---|---|
| 0 | 1005 | 70900 |
| 50 | 1054 | 1323 |
| 225 | 1274 | 1103 |
| 450 | 1158 | 1103 |

Figure 1. Height difference before and after SC1 clean bath for various amounts of Hydrogen Peroxide. Height increase indicates etching, height decrease indicates no etching and chemical growth of oxide.

In order to determine the amount of hydrogen peroxide necessary to prevent silicon etching in SC2, a six-inch silicon wafer with 1,000 angstroms of oxide was again coated, exposed, developed and etched. Following this the photoresist was removed. The Tencore P2 Profilometer was used to measure the height difference between the oxide and exposed silicon at a specific location at the center of the wafer. Next, the wafer was submerged in SC2for 15 minutes at 75 degrees Celsius containing 300 mL hydrochloric acid and 5,400 mL water. The Tencore P2 Profilometer was again used to determine the height difference between the oxide and silicon in the same previously measured location. The height difference decreased from 1,078 angstroms before submersion to 1,054 angstroms after submersion. A decrease indicates no etching and growth of a chemically grown oxide.

In order to determine that a 1:1 ratio of hydrogen peroxide to strong base or acid in SC1 and SC2 would produce working transistors, three six inch silicon wafers were taken through the PMOS process, as detailed on Dr. Fuller's website. Transistors on these silicon wafers were then tested after the process was completed, with results shown in Figure 2.

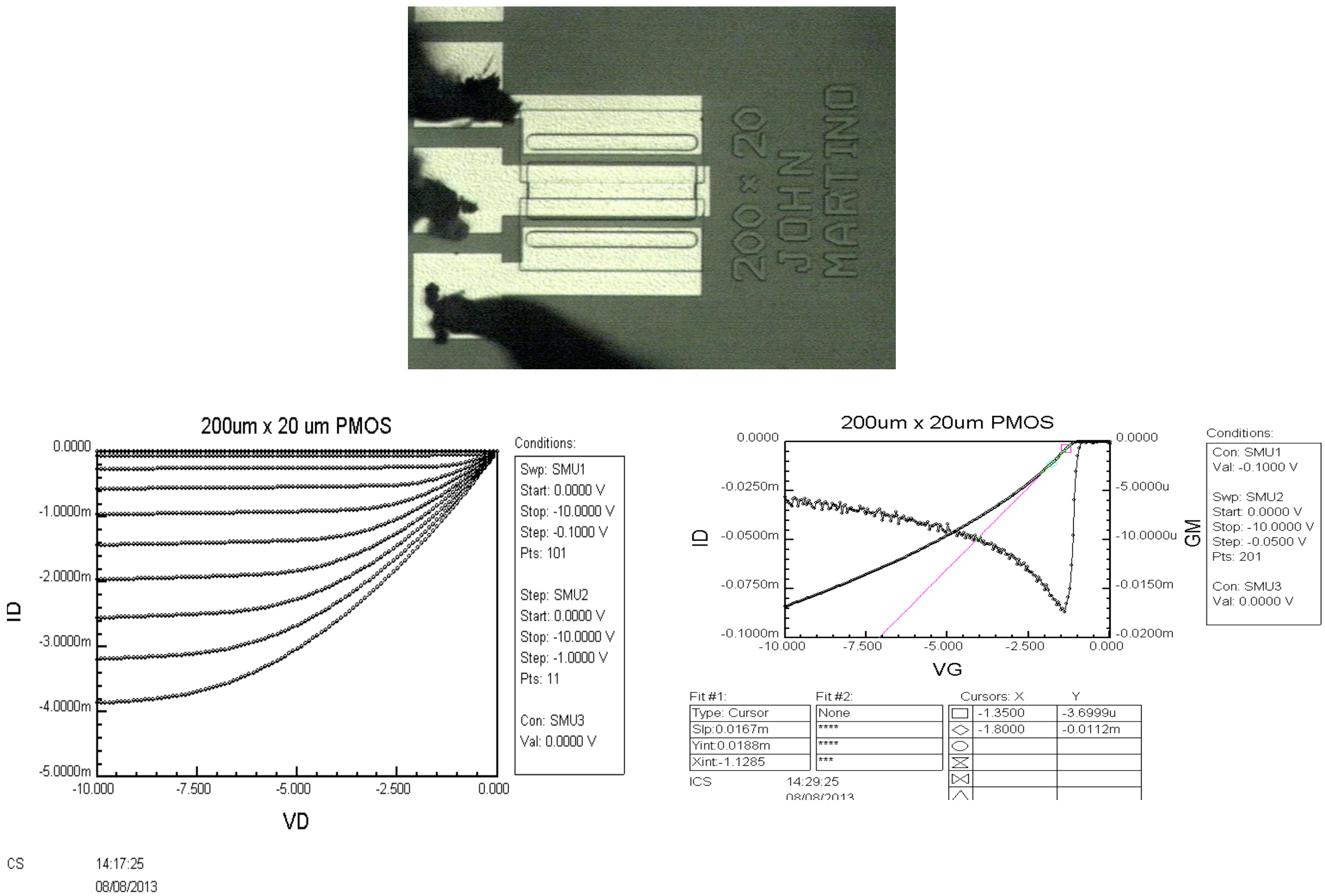



Figure 2. Electrical measurements on Metal Gate PMOS transistor. Shows excellent device characteristics with parameters comparable to previously made devices at RIT.

In order to determine the etch rate of the 50:1 HF, 1,000 angstroms of oxide were grown on a bare six-inch silicon wafer. The Spectramap was used to measure the oxide thickness at 81 points, producing an average of 1,011 angstroms with a standard deviation of 18 angstroms. The wafer was then submerged in the 50:1 HF bath for 60 seconds, rinsed and dried, and remeasured. The Spectramap produced an average oxide thickness of 864 angstroms with a standard deviation of 22 angstroms. Therefore 147 angstroms of oxide were etched in 60 seconds.

In order to determine the amount of oxide chemically grown during an RCA clean, a bare six-inch silicon wafer was submerged in a SC1 bath with 300 mL ammonium hydroxide, 900 mL hydrogen peroxide, and 4,500 mL water for 10 minutes at 75 degrees Celsius. The wafer was rinsed and placed in the 50:1 HF bath for 10 second increments until the wafer pulled dry, which occurred between 10 and 20 seconds.

## Discussion

In order to determine the amount of hydrogen peroxide that must be added to SC1of an RCA clean to prevent silicon etching, 4 six-inch silicon wafers were grown 1,000 angstroms of oxide and patterned. The height difference between oxide and silicon was measured before the wafers were submerged in SC1with 300 mL ammonium hydroxide, water, and varying amounts of hydrogen peroxide (0 mL, 50 mL, 225 mL, 450 mL) for 15 minutes at 75 degrees Celsius. The height difference between oxide and silicon was then measured again. When 0 mL and 50 mL of hydrogen peroxide were added to SC1, the height difference between oxide and silicon increased after submersion in the bath. Because neither ammonium hydroxide nor hydrogen peroxide affects oxide, the height difference can be attributed to the silicon on the wafer being etched by the ammonium hydroxide. This etching indicates that there was not enough hydrogen peroxide added to SC1to adequately protect the silicon wafer from etching. When 225 mL and 450 mL of hydrogen peroxide were added to SC1, the height difference between oxide and silicon decreased after the wafers were submerged in the bath. This indicates two things: the silicon was not etched and a chemically grown oxide was formed on the silicon. Had the silicon been etched, the oxide-silicon height difference would have increased after submersion in SC1, not decreased as was shown to happen. The decrease in height difference is evidence that a chemically grown oxide was formed, growing on top of the oxide and decreasing the measured step height. This part of the procedure supports the theory that a 1:1 ratio of ammonium hydroxide to hydrogen peroxide is sufficient to protect silicon wafers from etching, since 300 mL of ammonium hydroxide were added to SC1and yet 225 mL of hydrogen peroxide protected the wafer. This was supported when three six-inch silicon wafers were taken through the PMOS process, as detailed on Dr. Fuller's website. The transistors produced during this process functioned properly, indicating that the new chemical ratios in the RCA clean are effective at cleaning, since transistors are sensitive enough to not function properly if they were not cleaned effectively.

In order to determine the amount of hydrogen peroxide that SC2needs to protect silicon wafers from etching, the above procedure was repeated for a bath with 300 mL hydrochloric acid and 5,400 mL water for 15 minutes at 75 degrees Celsius. In this bath, which contained no hydrogen peroxide, the height difference between oxide and silicon slightly decreased, indicating that no etching occurred. This provides evidence that hydrochloric acid does not etch silicon, and adding hydrogen peroxide to SC2is unnecessary.

In order to determine how much chemically grown oxide is formed during an RCA clean, a bare silicon wafer was placed in SC1with 300 mL ammonium hydroxide, 900 mL hydrogen peroxide, and 4,500 mL water for 10 minutes at 75 degrees Celsius.. This wafer was then submerged in 50:1 HF for 10 seconds increments until it pulled dry. A wafer pulling dry, or water not remaining on the wafer surface after being pulled out of a water bath, indicates that it is bare silicon, since silicon is hydrophobic. Oxide is hydrophilic, so water will remain on the surface of silicon wafers with oxide when they are removed from water baths. The test wafer pulled dry after 20 seconds in the 50:1 HF bath, indicating that all of the chemically grown oxide had been removed to expose bare silicon. The 50:1 HF rate had been determined to be 147 angstroms/minute, or 2.45 angstroms/second. Therefore it was calculated that between 25 and 50 angstroms of chemically grown oxide was formed after 10 minutes in SC1. This provides evidence that the previous guideline of 60 seconds in 50:1 HF to remove all chemically grown oxide is incorrect. The dip time in 50:1 HF can be reduced to 30 seconds and still etch away all of the chemically grown oxide.

## Materials and Methods

**Patterning of Wafers for Use in SC1and SC2Experiments.** Six-inch silicon wafers were placed in the Bruce Furnace under recipe 311 to grow 1,000 angstroms of wet oxide at 900 degrees Celsius for 40 minutes. The SII Track was used to coat the wafers with photoresist, following which the first layer of PMOS Mask 13 was exposed using the ASML. The wafers were developed using the SSI Track and then submerged in 10:1 Buffered Oxide Etch for three minutes. Photoresist was removed with the Solvent Strip and wafers were rinsed and dried.

**Preparation of SC1Baths.** All SC1baths contained 300 mL ammonium hydroxide and enough water to bring the total bath volume to 5,700 mL. Each bath contained a different amount of 30% hydrogen peroxide: 0 mL, 50 mL, 225 mL, or 450 mL. Silicon wafers were placed in a teflon boat and were, one at a time, submerged in the bath for 15 minutes at 75 degrees Celsius. Once removed, wafers were rinsed for five minutes and placed in the Spin Rinse Dry.

**Preparation of SC2Bath.** The SC2bath contained 300 mL hydrochloric acid and 5,400 mL water. One silicon wafer in a teflon boat was submerged in the bath for 15 minutes at 75 degrees Celsius. Once removed from the bath, the wafer was rinsed for five minutes and placed in the Spin Rinse Dry.

**Oxide-Silicon Step Height Measurement.** The Tencore P2 Profilometer was used to measure the difference in height between the bare silicon and the oxide. The machine was loaded and calibrated according to the handbook's instructions and height measurement was performed by moving the measuring needle from oxide to silicon. The subsequent graph was leveled and step height was recorded.

**Determination of 50:1 HF Etch Rate.** The Bruce Furnace was used to grow 1,000 angstroms of wet oxide at 900 degrees Celsius for 40 minutes on a silicon wafer using recipe 311. The Spectramap was used to measure the oxide thickness for 81 points and produce a mean, standard deviation, minimum, and maximum. The wafer was then placed in a teflon boat and submerged in 50:1 HF for 60 seconds, rinsed for five minutes, and placed in the Spin Rinse Dry. The Spectramap was then again used to measure oxide thickness at 81 points.

**Determination of Thickness of Chemically Grown Oxide.** A bare six-inch silicon wafer was placed in SC1containing 300 mL ammonium hydroxide, 900 mL hydrogen peroxide, and 4,500 mL water for 10 minutes at 75 degrees Celsius. The wafer was then rinsed, submerged in 50:1 HF for 10 seconds, and submerged in water. Ten seconds dips in 50:1 HF followed by submersion in water were repeated until the wafer pulled dry from the water rinse.

**PMOS Process.** Three six-inch wafers were taken through the PMOS process as detailed on Dr. Fuller's website. The Short Course mask was used for all lithography and a 1:1 ratio of hydrogen peroxide to strong base or acid was used for all RCA cleans.