

## STUDIES OF CHLORINATED OXIDES

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### ABSTRACT

Three oxidation processes were employed to study the effects of chlorine on growth rate and device characteristics of capacitors. Oxide was grown without the use of TCA, with TCA prior to growth, and TCA during growth. An increased growth rate of the oxide, 450 angstroms in 42 minutes with TCA, as opposed to 50 minutes without TCA, was observed. Contrary to what was expected, the TCA processed oxides larger flatband shifts than the standard oxide growth wafers.

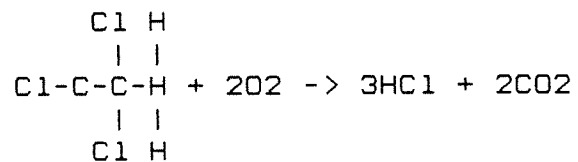
### INTRODUCTION

Chlorine has several effects when it is incorporated into the oxidation process. For a dry oxidation process, chlorine increases the oxide growth rate and improves the device characteristics. These improvements may include a reduction in oxide defects, which increases the SiO<sub>2</sub> breakdown strength, a reduction of the mobile charge, a reduction in the interface and fixed charge density and an increase in the lifetime of minority carriers[1].

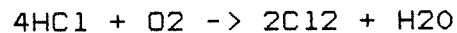
Mobile ion charge is minimized by reducing the introduction of Na ions to the oxide. Several sources of Na during processing are the oxidation and diffusion furnaces, incomplete resist removal and resist baking and contaminated cleaning chemicals. The furnace tubes can be cleaned of Na using chlorine at elevated temperatures. The chlorine is incorporated in the oxide at the Si/SiO<sub>2</sub> interface, neutralizing the Na ions.[3]

Safety is one of the concerns when using chlorine in the oxidation process. Possible chlorine sources include Cl<sub>2</sub> gas, HCl gas and trichloroethene (TCE) and trichloroethane (TCA). All of the chlorine sources are potentially hazardous. Chlorine gas is very toxic, TCE is a known carcinogen, and HCl is very corrosive when it absorbs water. The HCl can cause leaks by corroding the stainless steel fittings in the plumbing of the furnace. Trichloroethane (1,1,1) is the safest to use, although it can be dangerous if it is not used with an excess of oxygen. TCA can react and form phosgene, which is a deadly gas. The formation of phosgene can be reduced by using a low percentage of TCA in relation to the oxygen flow. That is why TCA is carried to the tube in N<sub>2</sub>, an inert gas. Other concerns are anisotropic etching of the substrates, which occurs when the chlorine flow is too high and the extra steps needed when using chlorine in the process [2].

Trichloroethane will be used in this project. The TCA reacts at high temperatures according to the reaction [4].



and then the HCl reacts in an excess of oxygen according to the reaction:



to produce the beneficial component Cl<sub>2</sub>.

The oxidation rate increases with the increasing concentration of HCl. The parabolic rate constant B, and also B/A increase with the addition of HCl. Water is formed when the HCl mixes with O<sub>2</sub> at the oxidation temperatures. The chlorine also increases the oxide growth rate when H<sub>2</sub>O is not present which implies that the chlorine is the primary factor in increasing the growth rate and not the formation of H<sub>2</sub>O. It is expected that the TCA clean will have no effect on the growth rate since the chlorine is not present in the tube during the oxide growth. The oxide growth rate should increase when the TCA is implored during the oxide growth.

## EXPERIMENT

Three gate oxidation processes were performed on 6 p-type and 6 n-type <100> wafers of resistivities 3 ohm-cm and 5 ohm-cm respectively. Two p-type and 2 n-type wafers were used for each process. For each process, the wafers were RCA cleaned, oxidized at 1000 degrees C, annealed for 20 minutes in 6 lpm of N<sub>2</sub>. Aluminum was evaporated on the front side of the wafers with minimal layover time between steps. This was done to keep the gates as clean as possible.

The first oxidation consisted of a 50 minute soak at 1000 degrees C with an O<sub>2</sub> flow of 5 lpm. This growth was repeated but a 3 hour TCA clean at 1100 degrees C was performed prior to the oxide growth. The temperature is increased to incorporate more chlorine in the tube therefore increasing the sodium ion passivation. The third process was the TCA oxide growth. The temperature of the tube was 1000 degrees C and the O<sub>2</sub> flow remained constant at 5 lpm. An initial protective oxide was grown for 10 minutes without TCA. The TCA bubbler was set to 25 degrees C and a 22 minute TCA growth was done with an N<sub>2</sub> flow of 190 sccm and an O<sub>2</sub> flow of 5 lpm. An O<sub>2</sub> purge was done for 5 minutes with an O<sub>2</sub> flow of 5 lpm.

Oxide thickness was measured using a Nanospec. A lithography step was done using the MOS capacitor mask which consists of die with 5 different capacitors. The capacitors

according to decreasing area are:  $1.645E-2$  cm<sup>2</sup>,  $7.9032E-3$  cm<sup>2</sup>,  $4.0323E-3$  cm<sup>2</sup> and two capacitors with area  $1.4516E-3$  cm<sup>2</sup>. The aluminum was etched. The front of the wafers were coated with resist and the back oxide was etched off to allow a good ohmic contact. Aluminum was evaporated on the backs of the wafers and the photoresist was ashed. The wafers were sintered in 6lpm of forming gas at 450 degrees C for 30 minutes.

The capacitors were initially tested by making C-V measurements on a Princeton Applied Research Model 410 C-V Plotter. Plots were made for the  $7.9032E-3$  cm<sup>2</sup> capacitor, measured on each wafer. The voltage was swept from -20 volts to +20 volts. The flatband voltage, threshold voltage, Cox and Cmin were determined on each curve.

### RESULTS/DISCUSSION

The oxide measured for each oxidation process was 450 angstroms. The soak times for the oxide with no TCA and TCA prior to growth was 50 minutes and the total soak time for the TCA oxide was 42 minutes.

The C-V data is listed in Table 1.

Table 1:  $7.9032$  cm<sup>2</sup> capacitors  
p-type

Theoretical	Without TCA	TCA prior to growth	TCA during growth
Cox 606	580	620	620
Cmin	260	300	270
Vt	-1.3v	-3.0v	-8.6v
Vfb	-2.2v	-4.6v	-11.4v
Cfb 293			

n-type

Theoretical	Without TCA	TCA prior to growth	TCA during growth
Cox 606	515	595	600
Cmin	100	100	110
Vt	-1.4v	-1.9v	-5.1v
Vfb	-0.6v	-0.7v	-4.4v
Cfb 286			

The C-V data was the exact opposite of what was expected. The flatband voltages for the TCA process were -11.4v and -5.1 volts for the p-type and n-type wafers respectively. These values were approximately 5 times more negative than the process which used no TCA. The oxide process with no TCA was expected to show the largest flatband shift.

Lifetime measurements were attempted but no measurements could be obtained. It is apparent that the C-V equipment available at RIT needs to be calibrated or updated since the theoretical and experimental Cox values varied so much. Since the original measurements were so questionable, no further measurements were made on these capacitors.

### CONCLUSION

The chlorine incorporated into the oxidation process did increase the oxide growth rate. The 450 angstrom target thickness was obtained in 42 minutes when the TCA was used during the growth, whereas the growth without TCA took 50 minutes to obtain 450 angstroms.

This project did not accomplish what was expected when comparing the device characteristics. The C-V measurements obtained were not what was expected. The chlorine did not improve the quality of the capacitors or the electrical properties. Also, the C-V measurement system at RIT needs to be calibrated in order to make accurate C-V measurements.

### ACKNOWLEDGMENTS

I would like to thank Mike Jackson for his assistance throughout this project.

### REFERENCES

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