

DEVELOPMENT AND EVALUATION OF CHLORINATED GATE OXIDES

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ABSTRACT

The effect of TCA tube cleaning and oxidation on mobile ion contamination for the growth of gate oxides was investigated. It was found that the TCA tube clean had a major effect in reduction of mobile ions, while the TCA gate oxide process employed had a negligible effect.

INTRODUCTION

It has been reported that chlorine doping can be used to improve the electrical performance of thermally grown oxides. Improvement over dry oxides has been reported in the following areas; 1) increased minority carrier lifetimes, 2) increased growth rates, 3) mobile ion passivation, 4) decreased size and density of oxidation induced stacking faults, and 5) increase in the average breakdown fields realized [1]. Possible drawbacks to a chlorinated oxide include complication of process, safety, degradation of oxide at very high chlorine levels, and possible etching of substrate in more highly doped areas.

There are many chlorine sources commercially available for use in the microelectronics industry, but the obvious choice for reasons of safety, ease of use, and purity is (1,1,1) Trichloroethane --> (TCA). Other possible sources include Cl₂ gas, HCl gas, and TCE (trichloroethene). TCA is much safer than either TCE or HCl chlorine sources. Using TCA eliminates the possibility of extremely costly HCl leaks caused by the corrosion of regulators, and the loosening of gas jungle fittings. As far as worker safety is concerned, TCA is the safest of the chlorine source chemicals. OSHA lists the PEL's of these chemicals as the following; J.C.S. TCA = 350 ppm, TCE = 100ppm, HCl = 5ppm [2]. Permissible exposure levels (PEL's) given above correspond to an employee's permissible average exposure in any eight hour shift of a forty hour week [2]. TCA also offers the advantage of being much cleaner than HCl. TCA can be made up to 99.9999% pure, many orders of magnitude lower in contamination than current electronic grade HCl [3]. TCA is not subject to the variability of contaminants such as iron and moisture which are common in HCl [2]. Purity is the factor cited in uniform and controlled growth of oxides with high dielectric strength and minority carrier lifetimes [2].

For this experiment a J.C. Schumacher TCA system was employed. This system uses nitrogen as a carrier gas for the TCA. The N₂ is bubbled through a temperature controlled bubbler apparatus and the TCA/N₂ mixture is combined with an excess of O₂

before entering the furnace.

The crux of the evaluation of the new gate oxide process will be in terms of the effect that chlorine in the oxide has on mobile ion (i.e. sodium) contamination. The hypothesis that chlorinated oxides offer the advantage of mobile charge gettering over dry O₂ growths will be investigated. The reduction in mobile charge seen in chlorinated oxides is said to work via sodium gettering in the oxide itself. The neutralization of positively charged mobile ions observed in TCA oxide is generally attributed to reactions of the mobile ions with the chlorine incorporated in the oxide as it is thermally grown. As far as exactly how the gettering works, the precise mechanisms of the mobile charge neutralization are not yet well understood. The best proposal at this point in time is that the mobile ions simply become trapped when they reach the vicinity of chlorine incorporated in a Si-O-Cl bond, where chlorine is substitutional for oxygen [4].

To determine if TCA does indeed getter Na⁺ ions, a C-V bias/stress test will be implemented on oxides grown by the dry O₂ process (pre tube clean), dry O₂ (post tube clean), and the new TCA process (post tube clean). In the bias stress test the wafer is heated to 200 degrees C. to facilitate the movement of mobile ions in the oxide. At the same time, a positive bias is applied to a particular MOS cap. The bias and the high temperature are held on the MOS cap for 5 minutes to insure complete movement of all mobile ions. The positive bias applied works to move all of the positively charged mobile ions away from the SiO₂/Al interface and toward the Si/SiO₂ interface. This has a tendency to shift the flatband voltage to the left, (toward more negative voltages). After 5 minutes, the chuck is cooled to room temperature and the bias is taken off of the MOS cap. A plot of C-V characteristics is then obtained to obtain a (-)V_{fb} value. The whole process is then repeated with a positive bias to yield a (+)V_{fb} value. The mobile ion density can then be computed using Equation (1) below:

$$Na^+ = (C_{ox}/q) \text{ ABS}(V_{fb(-)} - V_{fb(+)}) \quad (1)$$

where C_{ox} is computed using Equation (2), Na^+ is the mobile charge density in ions/cm², and the V_{fb} 's are obtained as described above from the bias stress C-V plots.

$$C_{ox} = C_{max}(\text{from CV plot}) / \text{Area of MOScap} \quad (2)$$

The effective mobile ion concentrations calculated using the above formulas will be compared, to determine if the new oxide process has indeed improved RIT's gate oxides and if the TCA tube clean has had any effect.

EXPERIMENT

A standard set of MOS caps was fabricated using the temperatures, times, gas flows, etc were all recorded and are contained in the process sheets found in Appendix II. (For a outline of all processes used see Appendix I.) The growth was basically a 1000 degree C., dry O₂, 1 hour oxidation followed by a N₂ anneal at the same temperature for 30 minutes. These conditions yielded an oxide thickness of approximately 650 Angstroms. These capacitors were then tested on a Princeton Applied Research (Model 410) high frequency C-V measurement system equipped with a Temptronic TP36 Thermochuck system, for the thermal stress bias test. First the MOS caps were measured to get a pre-stress C-V curve. The gate voltage was swept from (+)20 to (-)20 volts DC with a 1MHz AC signal. For consistency all measurements were taken with the lights on. After the pre-stress C-V curve was obtained, the MOS cap being evaluated was biased to -15 volts to move all of the mobile charge in the oxide to the SiO₂/Al interface. This bias remained applied while the wafer was heated to 200 degrees C. for 5 minutes. After the wafer was cooled back down to room temperature, the bias was removed and a second shifted C-V curve was obtained. The entire stress bias routine was then repeated with a +15 volt bias. Once again another shifted C-V curve was plotted on the same axis. The change in flatband voltage was then read from the C-V plots ((+) bias value - (-) bias value). This shift in flatband voltage was then converted to an effective total mobile ion concentration using the equations outlined in the theory.

The next step was to 'condition' the oxide tube with TCA so that existing mobile ion contamination would not effect the results of the TCA process. During the clean, temperatures were kept higher than the standard gate oxide temperatures to incorporate more chlorine in the tube, and in turn increase the efficiency of the mobile charge passivation taking place. Immediately after the tube was cleaned another set of wafers was oxidized with the current dry O₂ gate oxide process, as a means of a truly fair comparison with the TCA oxides.

In the final phase of the project 'new' MOS caps were fabricated using the new TCA gate oxide process (as outlined on the TCA gate oxide process sheets contained in Appendix I. This oxide was grown immediately following the second dry O₂ process in the cleaned tube to make the comparison truly valid. The 'new' MOS caps were then tested in the same manner as the 'old' MOS caps. The data obtained for the older gate oxide process MOScaps, was then compared to the data obtained for the new gate oxide process. Appropriate conclusions were drawn as to the effectiveness of the new TCA gate oxide process as far as mobile charge is concerned.

RESULTS AND DISCUSSION

The results shown in Table 1 indicated a 1.96×10^{12} ions/cm² (32%) improvement in mobile ion contamination after the tube clean (via comparison of the pre and post clean dry O₂ results). The TCA gate oxide process showed a reduction in mobile charge of $.07 \times 10^{12}$ ions/cm² (8%) over the standard dry O₂ gate oxide process. It is unlikely that the new TCA Gate oxide process reduced the effective mobile ion levels in the TCA MOS caps, as the standard deviation of the measurement was greater than the resultant improvement. However, it was clearly evident that the TCA tube clean employed did have a profound effect on reducing mobile ion levels.

Table 1 : Mobile Ion Levels and Vfb Shifts

Parameter	Process 1	Process 2	Process 3
Vfb shift	8.74 volts	2.76 volts	2.56 volts
Na ⁺ (ions/cm ²)	2.87×10^{12}	0.91×10^{12}	0.84×10^{12}
Na ⁺ Std. Dev.	0.23×10^{12}	0.14×10^{12}	0.12×10^{12}

Where;

Process 1 = standard process

Process 2 = standard process after TCA clean

Process 3 = TCA gate oxide process

Although the TCA gate oxide process had little effect on reducing mobile charge, the other possible benefits such as increased minority carrier lifetimes, increased average breakdown voltages, and decreased stacking faults should be evaluated before the process is ruled out as a viable alternative to the standard dry O₂ gate oxide process.

CONCLUSIONS

The TCA tube clean process was found to be an effective way of reducing mobile charge. Although the TCA gate oxide process employed was found to have little effect on mobile ion contamination in a single run, I recommend that the process should be used as a means of keeping the system clean between major tube cleans.

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REFERENCES

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- 2) "Product Application Note No. 5", J.C. Schumacher Company, 1986.
- 3) "Product Application Note # 14: TCA Requirements for thin High- Integrity Oxides.", J.C. Schumacher Company, 1986.
- 4) "Cl incorporation at the Si/SiO₂ interface during the oxidation of Si in HCl/O₂ ambients.", H.L. Tsai and others, Journal of the Electrochemical Society, February 1984, pp. 411-418.

APPENDICES

- Appendix I : Processes Employed
- Appendix II : Processing Sheets for MOS Caps
- Appendix III : Sample Experimental C-V Curves

APPENDIX I : Processes Employed

- I) Standard Dry O₂ Gate Oxide Process Parameters
 - Oxide Thickness Target; 650 Angstroms
 - Tube temperature; 1000 degrees C.
 - O₂ Flow Rate; 5 lpm.
 - Time; 60 minutes
- II) TCA Gate Oxide Process
 - Oxide Thickness Target; 650 Angstroms
 - Tube Temperature; 1000 degrees C.
 - Initial Dry O₂ Protective Oxide Growth
 - O₂ Flow Rate; 3.2 lpm.
 - Time; 10 minutes
 - TCA Oxide Growth
 - Bubbler Temperature; 25 degrees C.
 - N₂ Flow Rate; 160 sccm.
 - O₂ flow Rate; 3.2 lpm.
 - Time; 35 minutes
 - O₂ Purge
 - O₂ Flow Rate; 3.2 lpm.
 - Time; 5 minutes
- III) Gate Oxide Anneal
 - Tube Temperature; 1000 degrees C.
 - Time; 20 minutes
 - N₂ Flow Rate; 6 lpm.
- IV) TCA Tube Clean
 - Tube Temperature; 1100 degrees C.
 - Time; 3 hours
 - Bubbler Temperature; 25 degrees C.
 - N₂ Flow Rate; 250 sccm.
 - O₂ Flow Rate; 5 lpm.