Comparison of Ozone and Sulfuric Acid for Pre-Gate Oxidation Cleaning in the Manufacture of Analog Devices

Jason Taylor
Micrel Semiconductor
December, 2000

Abstract – The type of wet clean prior to gate oxidation is critical to the surface of the gate area prior to oxidation, affecting oxide integrity, and hence device performance. A study was made between standard sulfuric ("Piranha") cleaning and ozone cleaning prior to gate oxidation. Results showed comparable BVox levels between cleans, but significant yield increases were found using the ozone process. The environmental and other cost benefits of the ozone clean are also discussed.

INTRODUCTION

A comparison was made between a typical sulfuric "piranha" clean and an ozone type clean for pre-gate oxidation. The experiments were conducted to evaluate the feasibility of replacing the standard sulfuric pre-clean with an ozone clean. Ozone cleaning has the benefits of reducing cost of chemical purchase and disposal, energy cost reduction by eliminating hot (130 C) sulfuric acid, improving operator safety, decreasing cleaning cycle time, reducing thermal induced stress on the wafers, and providing a pure post-HF protective oxide growth. The environmental and safety benefits are significant on their own merits, but the primary objective in this study was to evaluate the difference in surface characteristics induced by the ozone clean verses the conventional hot sulfuric/peroxide, HF last pre-clean.

EXPERIMENT

Ten production lots of three different device types were used to evaluate the ozone clean. Two wet benches were used, one setup to run a typical sulfuric clean and oxide strip (HF last), and the other to run an ozone clean. The sulfuric clean process used was as follows: 10 minutes in 130 C sulfuric acid (spiked with 50 ml hydrogen just prior to cleaning), 5 minutes in a DI dump rinse, 10 seconds to 4 minutes in 10:1 HF (depending on device type), 5 minutes in a cascade DI rinse, followed by a spin rinse dry or an IPA dry (the type of drying was also investigated in this study). The ozone clean used was as follows: 5 minutes in DI/ozone (approximately 20ppm), 10 seconds to 4 minutes in 10:1 HF (depending on device type), 3 minutes in DI/ozone (approximately 20ppm), followed by a spin rinse dry or an IPA dry. The total clean time for the sulfuric process was about 30 minutes (including drying), and about 18 minutes for the ozone clean. The difference in time is due mainly to the increased oxidation capability of ozone (at room temperature), and the absence of a rinse step to remove the viscous sulfuric acid.

Two of the production lots were also used to test the addition of HCl (0.1%) in the final rinse for both cleans. The objective in adding HCl to the final rinse is to remove metallic contamination. It was not expected to have any serious metallic contamination with fresh chemicals, but the test was performed to evaluate the effect and provide a comparison for a future study of HCl addition after extended chemical use with known high levels of metallics.

The production lots were split into odd and even wafer numbers, odd wafers being processed with the ozone clean, and even wafers being processed with the sulfuric clean. In order to reduce sources of potential variation, cleaning was done on a single day, by the same operator, with the same batch of chemicals. Lots were recombined after the clean and loaded into the furnace together for oxidation. After completing the remaining fab process steps, the lots were electrically tested and sorted.

RESULTS AND DISCUSSION

Resulting yields and values of BVox are listed in Table 1, along with the percentage increase in yield due to the ozone clean. The mean yield values were verified to be statistically significant, at a 99% confidence level, by performing a Student's t-test. The only exception to an increase in yield occurred in the case of HCl addition, which actually showed a significant decrease in yield for the ozone clean compared to the sulfuric. The decrease in yield for HCl addition is suspected to be caused from the addition of too much HCl in the rinse, resulting in pitting of the silicon surface. Further studies will investigate the addition of varying levels of HCl over the full range of the chemical bath life.

Table 1: Summary of Results

Product Type	Split Info	Avg. Good Die	Std Dev	Ozone % Diff.	Avg. BVOX
A	1-25: sulfuric	734	32	-	44
A	26-50: ozone	750	27	**+2.1%**	42
A	1-25: sulfuric	566	38	**-**	49
A	26-50: ozone	576	32	**+1.7%**	42
A	26-50: sulfuric	737	48	**-**	47
A	1-25: ozone w/HCl	715	55	**-3.1%**	46
A	26-50: sulfuric	768	35	**-**	49
A	1-25: ozone w/HCl	735	61	**-4.5%**	47
B	26-50: sulfuric	792	37	**-**	41
B	1-25: ozone	805	41	**+1.7%**	41
C	odd: sulfuric	1591	49	**-**	44
C	even: ozone	1632	57	**+2.5%**	47
C	odd: sulfuric	1367	152	**-**	48
C	even: ozone	1424	88	**+4.0%**	48
C	odd: sulfuric	1225	174	**-**	48
C	even: ozone	1396	171	**+12.2%**	48
C	odd: sulfuric	1478	81	**-**	47
C	even: ozone	1530	73	**+3.4%**	46

The increase in yield was also verified over time, after the ozone clean was instituted as the standard pre-diffusion clean for all products, and resulted in significant annual revenue to the company. The additional benefits of reduced chemical purchase and disposal costs, energy costs, operator safety, and friendliness to the environment, combined to make the transition to an ozone-type clean a very significant improvement to the manufacturing of analog devices at Micrel.