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Advanced Si-Surface Preparation Techniques for Improved Gate Oxide Integrity

Marc M. HEYNS, Marc MEURIS, Steven VERHAVERBEKE, Paul W. MERTENS, Ara PHILIPOSSIAN¹, Dieter GRÄF² and Anton SCHNEGG²

IMEC, Kapeldreef 75, B-3001 Leuven, Belgium ¹Digital Equipment Corporation, 77 Reed Road, Hudson, USA ²Wacker-Chemitronic, D-8263 Burghausen, Germany

Abstract - Gate oxide breakdown is one of the major yield and reliability concerns in MOS technology. In this paper the influence of modified RCA pre-oxidation cleanings on the gate oxide integrity is investigated. The effect of the Si-surface roughening generated during the SC1-clean on the oxide characteristics is illustrated. Selective contamination experiments are used to investigate the effect of small amounts of contamination on the oxide breakdown. Finally, HF-last processes are investigated and some novel HF-processes are proposed.

1 - INTRODUCTION

Metal contamination and silicon surface roughness are important causes of defect-related gate-oxide breakdown in MOS-technology^{1,2}. Considerable improvements have been made over the last few years on the metallic contamination problems by using cleaner chemicals with fewer metal impurities. The origin and effects of Sisurface roughness on the gate oxide breakdown have been demonstrated¹ and considerable progress has been made in understanding and controlling this effect. This paper reviews some of the work which has been performed in IMEC on these topics over the last years.

2 - EXPERIMENTAL TECHNIQUES

The wafers used were <100> silicon wafers with a 125 mm diameter. Before the RCA-clean they underwent a 10 minute 5:1 H₂SO₄/H₂O₂ clean at 90°C, followed by a rinse in DI-water, a 20 s dip in 2% HF and another DIwater rinse. The RCA cleaning was performed in quartz containers. The SC1-step (NH4OH/H2O2/H2O) and SC2-step (HCl/H2O2/H2O) were both performed at 75-78°C for 10 min and immediately followed by a rinse in DI-water. The metallic contamination present on the wafer surface after cleaning or in the oxide after thermal oxidation was evaluated using the combination of vapor phase decomposition (VPD), droplet surface etching (DSE) with a 0.5% HF, 1% H₂O₂, 98.5% H₂O solution and total reflectance X-ray fluorescence (TXRF)³. Metals which can not be detected by TXRF were analysed using poly-encapsulated SIMS. For electrical characterization poly-Si gated capacitors were fabricated on the oxidized wafers. Typically oxidation was performed in dry O₂ (no chlorine added) at 900°C in a double-walled furnace tube to a thickness of 15 nm. Yield is defined as the percentage of capacitors surviving a field of 12 MV/cm.

3 - EFFECT OF CHEMICAL QUALITY

The metal content of the chemicals and the metal contamination on the silicon wafer after the SC1-clean were shown to have a linear correlation³. For typical cases this contamination level is determined by the purity of the hydrogen peroxyde. After the SC2-clean no such correlation could be detected and the metal contamination on the wafers after a complete RCA-clean using ULSIgrade chemicals from various vendors and with different metal content does not vary significantly and most metals are below detection limit. However, clear differences in the gate oxide integrity were observed which correlate with the difference in surface roughening behaviour in the SC1-clean of these chemicals³. When an SC1-only clean is used, a combination of this roughening effect and the metal contamination in the chemical oxide becomes the main cause of defect-related breakdown⁴.

4 - THE SC1-CLEAN

Experiments were performed to optimize the NH₄OH/H₂O₂/H₂O ratio in the SC1-clean⁴. The portions of peroxide and water were kept constant at 1:5 respectively while the portion of ammonia used was varied between 0.1 and 1. After the SC1-clean the iron concentration in the chemical oxide decreased as the ammonia content increased. If a subsequent SC2-step was performed all wafers showed an iron concentration around 3.1010 at/cm². For all other metals measured using VPD-TXRF the concentration was below 2.1010 at/cm². When higher ammonia portions were used the particle removal rate was enhanced but after 10 min all mixtures approached the same particle removal efficiency. In summary, both metal contamination and particle densities were equal after the complete RCA clean for wafers processed using all SC1-mixtures. From this one would normally expect similar breakdown

properties of subsequently grown gate oxides. However, a large difference was found in yield. The 0.25:1:5 SC-1 mixture results in much higher gate oxide integrity than the 1:1:5 mixture. The explanation for this can be found in the Si-surface roughness, as shown in fig.1, which clearly showed that the 1:1:5 mixture roughened the silicon surface much more than the 0.25:1:5 mixture did. A qualitative model for the action of the SC1-clean helps to understand the observations⁴. When silicon is exposed to the SC1-mixture, the peroxide will oxidize the silicon surface while the ammonia will etch this chemical oxide away; i.e. a chemical oxide layer will continually form and dissolve as a result of the compensating effect of the two chemical components. This slowly etches the silicon. A high etch rate will increase the particle removal efficiency by undercutting the particles, but causes a larger surface roughening during a 10 min clean. Consequently, one has to find an optimum between particle removal efficiency and silicon surface roughening. In our case this optimum was found at an etch rate of 0.2 nm/min. This point can be obtained by either changing the ammonia concentration or the temperature of the cleaning mixture, as shown in fig.2.

5 - METALLIC CONTAMINATION

Wafers were selectively contaminated with Al, Ca, Zn, Fe or Cu to levels of 10¹¹-10¹² at/cm² to study the effect of metals on the dielectric breakdown of thin thermal oxides^{5,6}. The measured concentration values of the intentional contamination before and after oxidation are shown in table 1. The Ca is found to be completely incorporated in the growing oxide during the oxidation step. The measured Ča levels after oxidation obtained on the other wafers show the existence of crosscontamination with Ca⁶. Upon oxidation Fe is partly incorporated into the oxide. Because of its relatively high diffusivity large amounts of Fe diffuses into the silicon. This is illustrated by the fact that further annealing reduces the Fe concentration⁶. The amount of Cu after oxidation is drastically reduced with respect to the initial contamination level of 1012 at/cm2. The final concentration of Cu always seems to end up at a constant level on the order of 10^{11} at/cm² within the contamination range under study. This is due to the high solubility limit and diffusion coefficient of Cu^{5,6}. The final Cu level after oxidation is completely determined by the precipitation at the surface during cool-down. Zn most likely diffuses into the silicon bulk or, in view of its high vapor pressure, may also partially evaporate in the oxidation furnace. Measurements of the dielectric breakdown performed on wafers from the same lot indicated that the breakdown statistics are dominated by Ca. Contamination with Fe also degrades the oxide quality⁵. Al has no effect on the oxide breakdown. The effect of Ca was found to be correlated with a large increase in Si-surface microroughness, characterized by the haze, which is generated on these wafers during the ramp up in an inert ambient (Ar). The haze drastically increases when the oxidation temperature is increased^{5,6}. Intrinsic gettering by performing a high-low-high temperature cycle can efficiently getter most metals, particularly Fe and Cu. This is illustrated in table 2. The

Ca contamination is largely unaffected by the gettering cycle. This is consistent with the fact that Ca is mainly located in the thermal oxide. From these results it can be concluded that for gate oxide integrity Ca is the most important contaminant. The Ca contamination can be avoided by using ultra-pure chemicals, ultra-pure DI-water, a carefully designed DI-water distribution system and by adding complexing agents to the cleaning solution such as EDTA⁵ or by HF-last cleaning.

6 - HF-LAST PROCESSES

After an HF-last cleaning the metallic contamination on the Si-surface is on the average lower than after an RCAclean for the typical metals found after a state-of-the-art cleaning. Only Cu can be problematic since it is the only metal which is present in an acid HF-solution with a higher half-cell potential than hydrogen and, therefore, can be deposited on the Si-surface from an HFsolution⁷. This can be avoided by using ultra-pure chemicals or by adding small amounts of H2O2 to the HF-solution⁸. Typical results are shown in tables 3 and 4. Al was not detected above the detection limit of 5.109 at/cm². In table 3 no significant difference in Cu contamination is observed upon addition of H2O2 to the HF-solution. Only the BHF case shows an important Cu contamination. The beneficial effect of a DI-water rinsing on the concentration of alkali's is clearly illustrated in table 4. Due to their low metallic contamination HFdipped surfaces are well-suited for the growth of highlyreliable thin gate oxides. However, hydrophobic surfaces are well known to be susceptible to particle deposition. Therefore, the proces has to be carefully optimized. The contact angle of a droplet of DI-water on the Si-surface was used to investigate the surface chemical condition as a function of dipping time in diluted HF-solutions before after subsequent rinsing in DI-water. These contact angle measurements were correlated with XPS-results9 and were found to be very sensitive to the remaining fraction of oxide on the Sisurface (down to 1/10 of a SiO2 monolayer). It was observed that full passivation of the Si-surface (and the corresponding large contact angle of more than 70°C) can be reached by either prolonging the time of the HF-dip, by adding minute amounts of IPA to the HF-solution¹⁰ or by changing the temperature of the HF-solution9. This does not drastically change the nature of the Si-surface but prevents the deposition of particles on the Si-surface during HF-dipping and subsequent rinsing and results in highly reliable oxide layers.

7 - CONCLUSIONS

Some aspects of the pre-oxidation cleaning were studied. The ammonia content in the SC1 cleaning mixture must be choosen at an optimum between particle removal and Si-surface roughening. Ca contamination was found to strongly degrade the gate oxide integrity. Contact angle measurements are a sensitive probe to investigate the Sisurface after HF-dipping. The addition of small amounts of IPA to the HF-mixture or increasing the time or temperature of the HF leads to a more fully passivated Si-surface with lower particle adhesion.

8 - REFERENCES

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Table 1 : Metal contamination $(10^{10} \text{ at/cm}^2)$ on the intentionally contaminated wafers. The results obtained on the different wafers are tabulated in the same order as the wafers were placed in the oxidation furnace.

1	b	efore o	oxidatio	on	
int. contamination	Ca	Fe	Cu	Zn	
blank	6	2	0.6	15	
10 ¹² at/cm ² Zn	2	1	1	80	
10 ¹² at/cm ² Fe	3	100	0.6	1	
1012 at/cm2 Ca	85	0.9	0.3	0.6	
1012 at/cm2 Cu	4	3	140	2	
10 ¹¹ at/cm ² Cu	11	16	18	2	
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		after o	xidatio	n	===
int. contamination	Ca	after o Fe	xidatio Cu	n Zn	
int. contamination blank	<u>Ca</u> 12	after o Fe 1	xidatio Cu 17	n Zn 3	
int. contamination blank 10 ¹² at/cm ² Zn	Ca 12 18	after o Fe 1 48	xidatio Cu 17 13	n Zn 3 11	
int. contamination blank 10 ¹² at/cm ² Zn 10 ¹² at/cm ² Fe	Ca 12 18 40	after o Fe 1 48 28	xidatio Cu 17 13 6	n Zn 3 11 2	
$\frac{\text{int. contamination}}{\text{blank}}$ $10^{12} \text{ at/cm}^2 \text{ Zn}$ $10^{12} \text{ at/cm}^2 \text{ Fe}$ $10^{12} \text{ at/cm}^2 \text{ Ca}$	Ca 12 18 40 140	after o Fe 1 48 28 1	xidatio Cu 17 13 6 7	n Zn 3 11 2 1	
int. contamination blank 10^{12} at/cm ² Zn 10^{12} at/cm ² Fe 10^{12} at/cm ² Ca 10^{12} at/cm ² Cu	Ca 12 18 40 140 10	after o Fe 1 48 28 1 1 1	xidatio Cu 17 13 6 7 17	n <u>Zn</u> 3 11 2 1 0.4	

Table 2 : Metal contamination $(10^{10} \text{ at/cm}^2)$ after preoxidation cleaning, after growing a 13 nm oxide at 950°C and after thermal oxidation preceded by a heat cycle to create an intrinsic getter (IG).

condition	measurements						
	Ca	Cr	Mn	Fe	Ni	Cu	Zn
before ox.	8	0.2	0.1	7	0.3	1.4	4
13 nm ox.	11	1.5	0.4	4	0.2	4	0.4
IG+13nm	13	0.2	< 0.1	1.1	< 0.1	1.8	0.3

Table 3 : Typical metallic contamination after different last cleaning steps followed by rinsing $(10^{10} \text{ at/cm}^2)$.

	K	Ca	Cr	Fe	Ni	Cu	Zn
RCA	0.3	8.6	0.2	5.1	3.3	0.3	0.4
HF	0.1	3.8	0.05	0.3	0.1	0.06	0.1
HF/H ₂ O ₂	0.6	1.6	0.3	2.2	0.2	0.09	1.2
BHF	0.2	1.4	0.4	2.6	0.3	3.7	0.7

Table 4 : Typical metallic contamination after different last cleaning steps $(10^{10} \text{ at/cm}^2)$ measured by poly-encapsulated SIMS.

	K	Na	Mg	Al
RCA+rinse	0.6	1.4	0.2	<1.0
HF	1.0	1.0	0.04	<1.0
HF+rinse	0.2	0.3	0.02	<1.0



Fig. 1: Atomic Force Microscopy measurements on wafers cleaned in (a) 1:1:5 and (b) 0.25:1:5 NH₄OH/H₂O₂/H₂O mixtures.



Fig. 2: Etch rates for 0.25:1:5 and 0.05:1:5 SC1mixtures as a function of the temperature.