

## The Importance of H<sub>2</sub>O<sub>2</sub> Decomposition in Silicon Surface Cleaning

H.F. Schmidt<sup>a</sup>, M. Meuris<sup>a</sup>, P.W. Mertens<sup>a</sup>, A.L.P. Rotondaro<sup>a</sup>,  
M.M. Heyns<sup>a</sup>, T.Q. Hurd<sup>b</sup> and Z. Hatcher<sup>c</sup>

<sup>a</sup>IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

<sup>b</sup>Texas Instruments, Dallas, TX, U.S.A., presently at IMEC

<sup>c</sup>Ashland Chemical, Columbus, OH, U.S.A.

In this study we have investigated the impact of temperature and metal contamination on the stability of hydrogen peroxide in the two most common wet chemical cleaning mixtures for wafer process operations. The caustic mixture (SC1) was found to be very sensitive to certain metallic contaminations in the sub-ppb range, while the stability of the acid mixture (SC2) is mainly influenced by non metallic, anionic components of the solution itself. We also found, that the oxygen gas bubbles, formed by the decomposition of hydrogen peroxide cause surface micro-roughness through a micro masking mechanism which has a significant impact on the integrity of thin gate oxides.

### 1. Introduction

For nearly 30 years, wet cleaning chemistry for wafer processing operations has been based mainly on the mixing of hydrogen peroxide with ammonium hydroxide (SC1 mixture) and hydrochloric acid (SC2 mixture). Even additional cleaning steps, carried out to improve the cleaning efficiency contain H<sub>2</sub>O<sub>2</sub> as one active component, e.g. sulphuric acid/hydrogen peroxide (SPM) and hydrofluoric acid/hydrogen peroxide [1,2]. This preference for H<sub>2</sub>O<sub>2</sub> is based upon its unique properties as it is a very strong oxidising agent, has no by-products except water and oxygen, and is of itself very stable if critical impurities are kept low. Once H<sub>2</sub>O<sub>2</sub> is mixed with other reagents and is exposed to certain metallic and non-metallic impurities, even in the low ppb range, its stability can suffer dramatically and the reliability of the cleaning bath goes down [3].

### 2. Hydrogen Peroxide Decomposition and Surface Roughness

The SC1 cleaning step is applied in order to remove particles from the wafer surface by an under etching and lift off mechanism. In sensitive light scattering measurements particles show up as LPD's (light point defects) together with other surface irregularities. Under certain conditions a large increase in small LPD's is observed after SC1 cleanings. In our work we have found that these LPD's and their formation mechanism is related to the gas bubbles created by the decomposition of H<sub>2</sub>O<sub>2</sub> which releases oxygen. By applying atomic force and scanning electron microscopy, we identified these LPD's as small silicon spikes (Fig. 1), which were caused by small oxygen gas bubbles blocking the

wafer surface from the etching action of the SC1 chemistry.

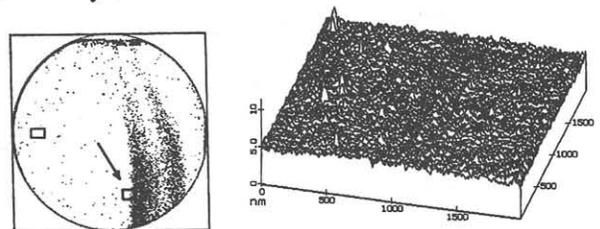


Fig. 1: AFM plot from the part of a wafer which showed decomposition patterns when measured for sensitive light scattering with a Censor ANS100.

This micro-roughening effect only occurs on wafers which are hydrophobic before being immersed into the SC1 solution. By monitoring the rate by which oxygen gas is released in real time with a gasometric technique it is possible to correlate the "oxygen evolution rate" of an SC1 mixture with the addition of LPD's on a wafer surface. This is shown in Fig. 2.

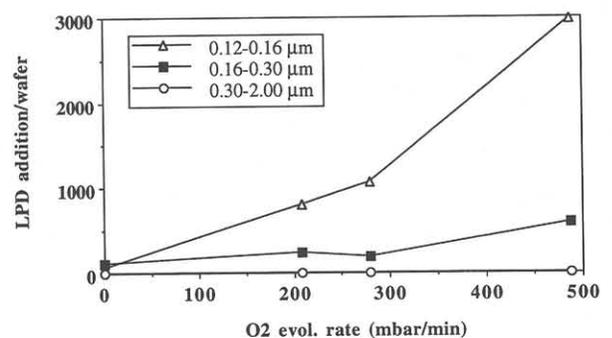


Fig. 2: Correlation between oxygen evolution rate and LPD addition on hydrophobic wafers.

LPD's below  $0.16 \mu\text{m}$  show a strong, nearly linear correlation with the initial oxygen evolution rate, while LPD's between  $0.16$  and  $0.30 \mu\text{m}$  are only slightly affected. No influence could be found for LPD's above  $0.3 \mu\text{m}$ . In Fig. 3 the decomposition behaviour of an SC1 mixture with  $\sim 1\text{ppb}$  of metallic contamination in total solution is shown as a function of the time.

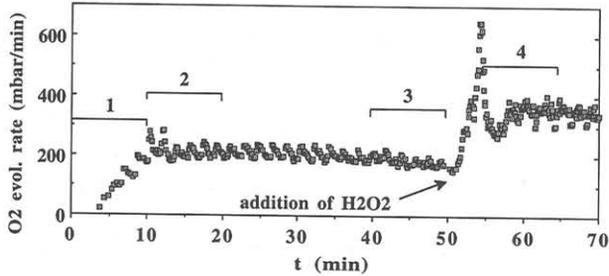


Fig. 3: Typical decomposition behaviour of an SC1 mixture at  $70^\circ\text{C}$  with a contamination level of  $\sim 1\text{ppb}$  of metallic contamination in total SC1.

Four cassettes with pre-cleaned, metallic contamination free, hydrophobic wafers were immersed one after another in this bath for 10 minutes. The immersion times are marked in Fig. 3 with numbered horizontal bars. Between the third and the fourth cassette, the SC1 mixture was re-spiked with  $\text{H}_2\text{O}_2$  to obtain the initial mixing ratio. As a result of the addition of  $\text{H}_2\text{O}_2$  the oxygen evolution rate increased very strongly, which also yielded a higher number of LPD's added on wafers immersed at this point. The sensitive light scattering maps of representative wafers from the four cassettes of this experiment are shown in Fig. 4.

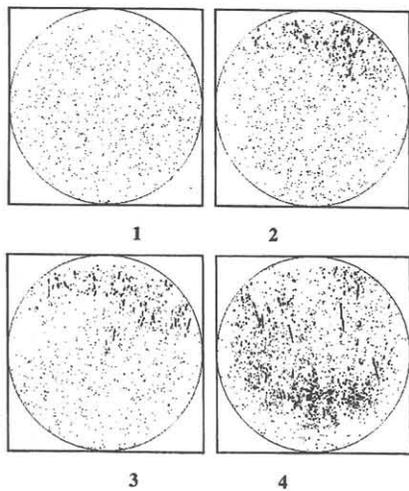


Fig. 4: Typical decomposition patterns from the 4 consecutively cleaned cassettes of wafers (labelled from 1 to 4 in Fig. 3).

### 3. Hydrogen Peroxide Decomposition and Gate Oxide Integrity

Fig. 5 and Fig. 6 are showing LPD maps of wafers with typical decomposition patterns after cleaning and gate oxidation and the resulting analog  $E_{bd}$  wafer mappings after build up of poly-gate capacitors. This significant impact on GOI was found

on p-type CZ and EPI substrates with  $6.5\text{nm}$  and  $15\text{nm}$  oxides. A summary of the  $E_{bd}$  yields of large capacitors on these substrates is shown in Fig. 7.

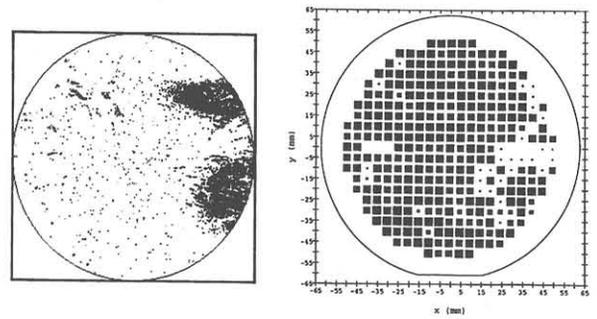


Fig. 5: Correlation between decomposition patterns and the resulting  $0 - 18\text{MV/cm}$  analog  $E_{bd}$ -yield plot. The largest black squares are symbolising good capacitors while the smallest ones are symbolising early break down events (capacitor area= $15.8 \text{mm}^2$ ,  $15\text{nm}$  gate oxide, p-CZ substrate).

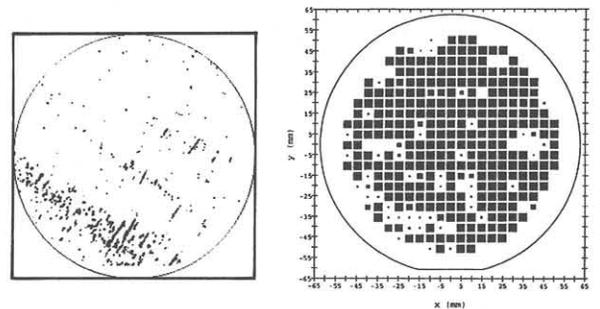


Fig. 6: Correlation between decomposition patterns and the resulting analog  $E_{bd}$ -yield plot (capacitor area= $15.8 \text{mm}^2$ ,  $15\text{nm}$  gate oxide, p/p+ EPI substrate).

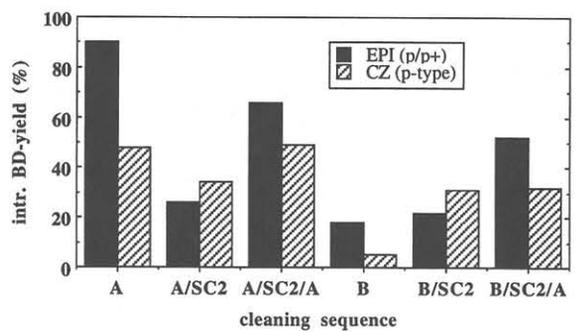


Fig. 7: Intrinsic  $E_{bd}$ -yield as a function of the cleaning sequence (area= $15.8 \text{mm}^2$ ,  $6.5\text{nm}$  gate oxide,  $>12\text{MV/cm}$ ). "A" symbolises a high quality SC1, "B" a low quality SC1 step.

"A" represents an ultra pure SC1 mixture with a very low decomposition rate (metal impurity level  $<0.2 \text{ppb}$ ), while "B" represents a vigorously decomposing SC1 mixture with an impurity level of  $\sim 1\text{ppb}$  of

metallic contamination in the solution. After the full cleaning sequences A/SC2/A and B/SC2/A, all wafers end up with the same metal contamination on their surface, but they are different in their LPD counts. The wafers from the B/SC2/A sequence show an order of magnitude higher LPD's (arranged in typical decomposition patterns) than the A/SC2/A reference wafers. Correlating to this, the  $E_{bd}$  yields are lower as well.

#### 4. Influences on the Decomposition Rate of Hydrogen Peroxide

The stability of  $H_2O_2$  is influenced by both metallic and non-metallic contaminants, the temperature and the pH of the solution. Fig. 8 shows the impact of the temperature on the stability of  $H_2O_2$  in an ultra pure SC1 mixture which is following the Arrhenius equation.

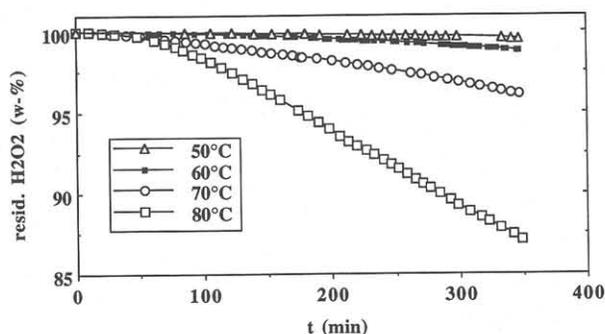


Fig. 8: Decrease of the  $H_2O_2$  concentration in an ultra pure SC1 mixture with time as a function of the bath temperature (metal contamination  $< 0.2$  ppb).

From this we calculated an activation energy of 102.6 kJ/mol for the decomposition of  $H_2O_2$  in this specific SC1 mixture. The half life, which is the time until 50% of the initial  $H_2O_2$  decomposes, increases from 21 hours to 44 days by reducing the temperature from 80°C to 50°C. The same trend is obtained with  $H_2O_2$  in an SC2 mixture where we found an half life increase from 18 min to 3.3 hours by reducing the temperature from 80°C to 50°C (Fig. 9). In Fig. 10, the impact of metallic impurities on the decomposition rate of an SC1 mixture is shown.

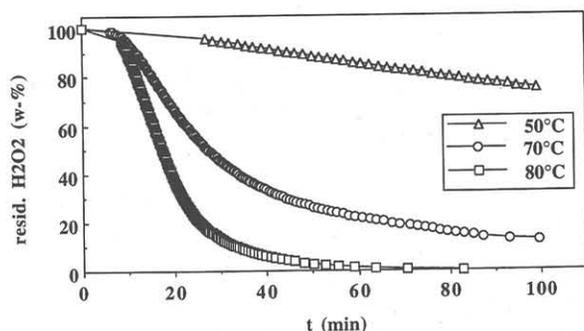


Fig. 9: Decrease of the  $H_2O_2$  concentration in an SC2 mixture with time as a function of the bath temperature (metal contamination  $\sim 1$  ppb).

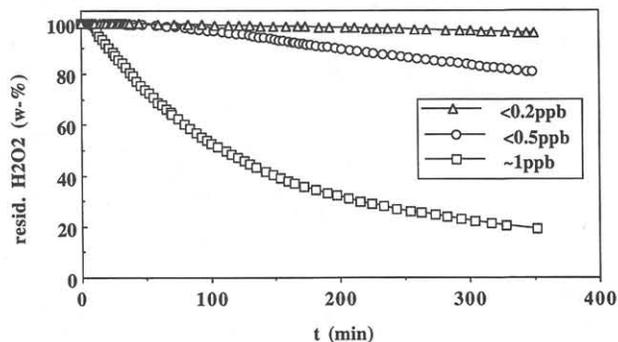


Fig. 10: Decrease of the  $H_2O_2$  concentration as a function of the metal contamination level in the SC1 mixture at 70°C.

The half life decreases from 2 days to 100 min with increasing metal contamination in the sub-ppb range. Especially  $Fe^{3+}$  and  $Cu^{2+}$  were found to be very effective in de-stabilising an SC1 mixture. This dependence was not found in an SC2 bath (Fig. 11).

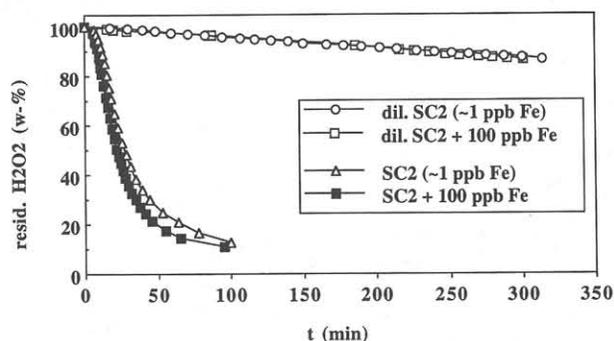


Fig. 11: Influence of the HCl and  $Fe^{3+}$  concentration on the stability of an SC2 mixture at 75°C.

An SC2 mixture shows nearly no reaction to  $Fe^{3+}$  contamination (we spiked up to 100 ppb), but it is very sensitive to the  $Cl^-$  and  $H^+$  concentration. Reducing the HCl concentration by a factor of 10 results in a half life of around 19 hours, while in a standard SC2 mixture the half life of the  $H_2O_2$  is less than 20 minutes. The reason for this is most likely the activity of the  $Cl^-$  as a decomposition catalyst and also the presence of  $Br^-$  in the HCl, which is also known as a catalyst for the decomposition of  $H_2O_2$ .

#### 5. Conclusion

While the stability of  $H_2O_2$  in an SC2 mixture seems to be only of economic interest, it is of great concern in an SC1 mixture because it causes surface micro-roughness, which has direct impact on GOI.

#### 6. References

- [1] W. Kern: J. Electrochem. Soc. **137** (1990) 1887.
- [2] T. Ohmi et al.: J. Electrochem. Soc. **140** (1993) 811.
- [3] H.F. Schmidt, et al.: Proc. 3rd Int. Symp. Cleaning Technology in Semiconductor Device Manufacturing, 1993 (The Electrochem. Soc., Penning ton, NJ, 1994) p. 102.