

Effect of pH Values in Ozonized Ultrapure Water on Cleaning Efficiency

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New cleaning methods are required to satisfy lowering cost of ownership (CoO) and promoting Environment, Safety and Health (ESH) in semiconductor manufacturing. The ozonized ultrapure water (O₃-UPW) with the economic benefits became to play an important part in current wet cleaning [1]. However, the cleaning efficiencies for removing contaminants such as noble metals and organic contaminants, and etc, should be much improved, compared to those of typical cleanings [2].

Figure 1 shows the dependence of copper (Cu) removal efficiency on the exposure time in clean room after the contamination. The removal efficiency from the surface has a big difference with the times. Even though the O₃-UPW is well known to chemicals with the impurity removal efficiency, the cleaning on the surfaces with delaying time after contamination is not effective in our study.

Figure 2 compares the x-ray photoelectron spectroscopy (XPS) spectra of the Cu contaminated Si surfaces. Judging from the ghost peaks on increasing exposure time, the surface of contaminated copper seems to be oxidized more and more. We points out that the surface oxidation on the Cu strongly affects the removal efficiency of the cleaning method. That is, the O₃-UPW with a high oxidation-reduction potential (ORP) value doesn't have the capability to remove the oxidized Cu impurities from the surface. This is attributed to the pH value of the solution, which has almost neutral pH value of 6.5: close vicinity to phase boundary of Cu ions and CuO in solution. It is therefore mandatory to decrease the pH value to improve the impurity removal efficiency from substrates. Figure 3 represents the influence of pH and ORP values in the solution on the removal efficiency. The pH value of the solution was controlled by method of adding CO₂ to O₃-UPW. The cleaning with a pH 4 can remove the impurities below 10¹¹ atoms/cm².

Figure 4 shows the removal efficiency of organic contaminants with various cleaning solutions. The amount of organic contaminants is determined by use of a fourier transform infrared reflectance-attenuated total reflection (FTIR-ATR) with germanium as a prism material. The hydrocarbon signals from the silicon surface are observed around the wave number of 2900 cm⁻¹. The removal efficiency of new CO₂ added O₃-UPW is much superior to that of other cleanings.

Figure 5 is showing the pH and ORP values of various solutions. In general, the ORP values in solutions increase with the decrease of pH value at same solution. The O₃-UPW has much high ORP value on adding CO₂ to the solution. The increase can affect the organic contaminants removal from Si surface (fig.4). Based on our results from metallic impurity and organic contaminants removal from wafer surface, we propose CO₂ added O₃-UPW instead of O₃-UPW only, so that, the 4-step room temperature cleaning is changed into Table 1.

The room temperature cleaning, based on the pH controlled O₃-UPW, can be easily applicable for the state-of-art cleaning.

References

- [1] T. Ohmi, in Proc. of SPWCC, March, 2000.
- [2] I. Yokoi, et al., in Proc. of SSDM, August, 2000.

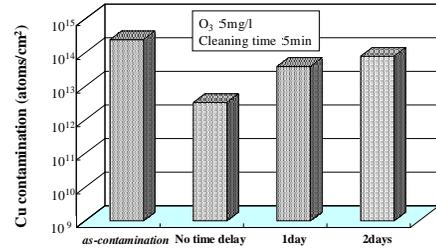


Fig.1. The dependence of Cu removal efficiency of O₃-UPW.

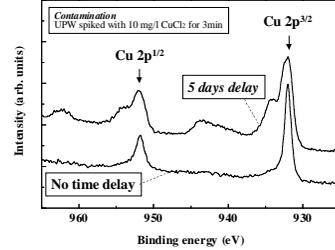


Fig.2. XPS spectra of Cu contaminated silicon surface on exposing time in cleanroom.

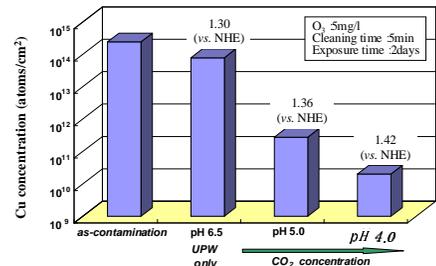


Fig.3. The dependence of Cu removal efficiency on pH and ORP values in CO₂ added O₃-UPW.

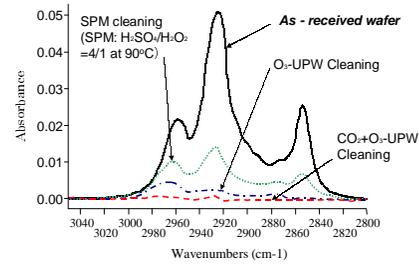


Fig.4. FTIR-ATR spectra of remaining hydrocarbon on silicon surface.

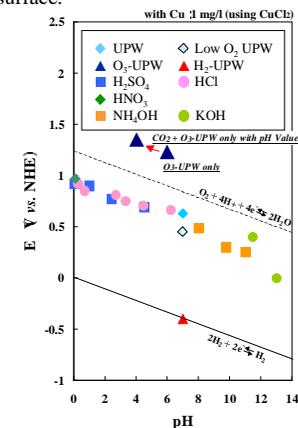


Fig.5. pH and ORP values of various solutions.

Target	Cleaning Sequence
Organic Metal	CO ₂ + O ₃ -UPW (pH=4.0)
Particle	NH ₃ + H ₂ -UPW with MS (pH=9.3-10.0)
Metal	FPM (HF/H ₂ O ₂)
Rinse	H ⁺ Radical added UPW

(MS Megasonic)

Table 1. 4 steps room temperature wet cleaning.