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Post-Metal-CMP Cleaning Using Oxalic Acid

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1. Introduction

Post-metal-CMP cleaning process needs the high removal efficiency of particles and metallic contaminations, without etching or degrading the interconnection metals and interlayer dielectrics. It has been difficult to achieve these requirements simultaneously, especially for low dielectric constant interlayer films such as HSQ (hydrogen silsesquioxane), and for new interconnection metals such as Cu. For particle removal without degradation of the Cu and the HSQ films of the damascene structure, we have reported a post-CMP cleaning process using electrolytic ionized ultra pure cathode water (pure-EIW).[1] There is an additional problem: metallic contamination. The residual metallic contamination on the HSQ film induces the increase in the leakage current of HSQ. In order to clean up the metallic contamination, we propose a cleaning process by using an effective cleaning solution, oxalic acid. The oxalic acid performs the high chelating effect with various metallic contaminations to form the metal complexes. With our technique, Cu contamination could be cleaned up without degrading the Cu interconnection and the HSQ film.

2. Device structure and experiments

Figure 1 shows a schematic diagram of a Cu/HSQ structure after Cu-CMP. A barrier metal is used to prevent Cu diffusion from Cu interconnection into Si substrate or HSQ layer. Cu contamination, however, takes place on the HSQ layer due to Cu-CMP. The Cu contamination must be removed to avoid degradation of device characteristics.[2]

Figure 2 shows the proposed cleaning process. In the first step, brush-scrubbing using pure-EIW was employed for particle removal after Cu-CMP. In the second step, a spin-spray cleaning was used with oxalic acid, $(COOH)_2$. The metallic concentration was analyzed by TRXRF.

3. Results and Discussion

Table 1 shows the etching rate of HSQ film and Cu film using various solutions and shows the change of the dielectric constant of HSQ film by various treatments. Treatments with conventional chemicals, diluted NH_4OH and diluted HF, cause higher etching rates of HSQ and Cu, as well as degradation of the HSQ dielectric constant. In contrast, pure-EIW and oxalic acid do not cause any degradation of Cu and HSQ films.

The Cu contamination on the HSQ film after Cu-CMP was in the range of more than 10^{12} atoms/cm^2. The pure-EIW, even though effective for particle removal, can not remove Cu contamination. Figure 3 shows the Cu-contamination removal efficiency by using spin-spray cleaning with oxalic acid of various concentrations. Cu contamination can be removed to the level of the TRXRF detection limit, $<10^{10}$ atoms/cm^2, by using oxalic acid of >0.3 %. Contamination of other metals, such as K, Ca, Ti, Fe, Cr, Ni, Zn was also reduced to $<2\times10^{10}$ atoms/cm^2 by the 0.3 %-oxalic acid cleaning as shown in Fig. 4.

Figure 5 shows schematically the mechanism of Cu contamination by using oxalic acid. Cu contamination on the HSQ film surface is supposed to form CuOx. The reaction between oxalic acid and CuOx forms $[Cu(COO)_4]^{2-}$, which is easily dissolved in the solutions. In contrast the bulk metal-Cu of interconnection does not react easily with the oxalic acid. Thus the Cu interconnection is not etched by the oxalic acid.

Figure 6 shows the leakage current of HSQ film after 400℃ annealing for 30 min. The leakage current of HSQ film after oxalic acid cleaning is one order of magnitude less than that before cleaning with a Cu residue of 5×10^{12} atoms/cm^2. Therefore oxalic acid cleaning is effective to improve the reliability of the HSQ interlayer.

4. Conclusions

The post-Cu/HSQ-CMP cleaning using the oxalic acid with high chelating effect successfully removed Cu contamination and other metals without etching the Cu interconnection and without degrading the HSQ film. Such new post-CMP cleaning process is a significant process for the metal-CMP and the low-K-film-CMP of next generation devices.

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References

1) H. Aoki et al., Proc. of IEDM. Tech., (1997) 777.
2) Alvin l. S. Loke et al., IEEE Trans. EDL, Vol. 17, No. 12 (1996) 549

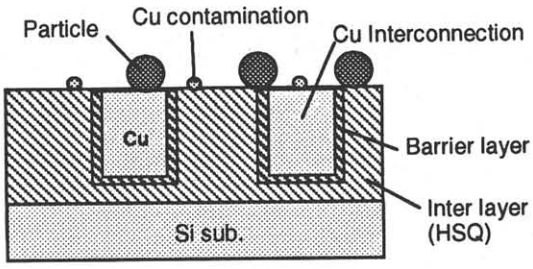

Fig. 1. Schematic diagram of a Cu/HSQ structure after Cu-CMP.

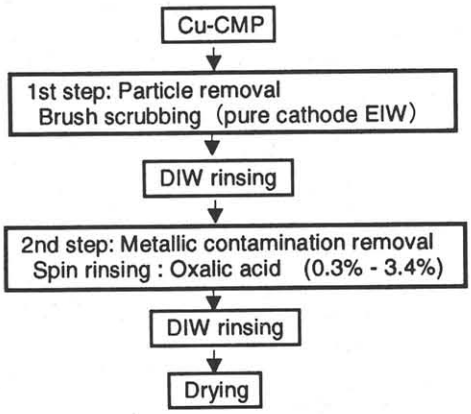

Fig. 2. A proposed post-CMP cleaning process.

Table 1. Etching rate of HSQ film and Cu film using various solutions, and the change of dielectric constant of HSQ film by various treatments.

Cleaning Solution	HSQ Etching Rate (nm/min)	HSQ Dielectric constant	Cu Etching Rate (nm/min)
DHF (0.5%)	252	2.9 → 3.7	1
NH4OH (1.8%)	4	2.9 → 4.8	8
Pure-EIW	<0.1	2.9 → 2.9	<0.1
Oxalic acid (1%)	<0.1	2.9 → 2.9	<0.1

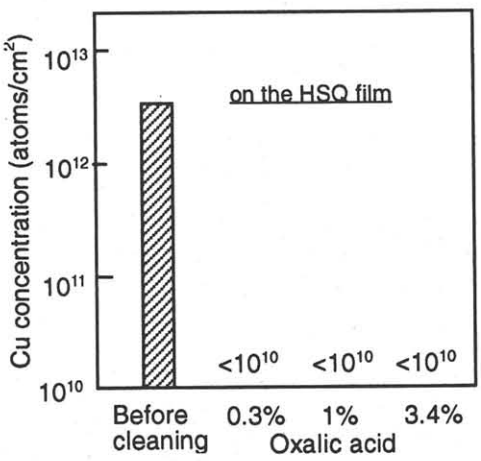

Fig. 3. The dependence of Cu contamination removing ability on oxalic acid concentration using spin cleaning.

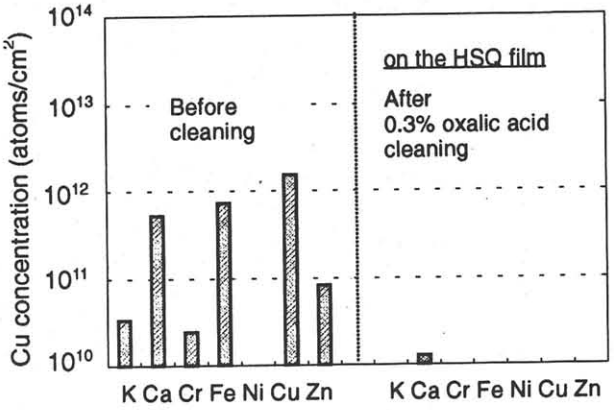

Fig. 4 Metallic contamination on the HSQ film surface after Cu-CMP.

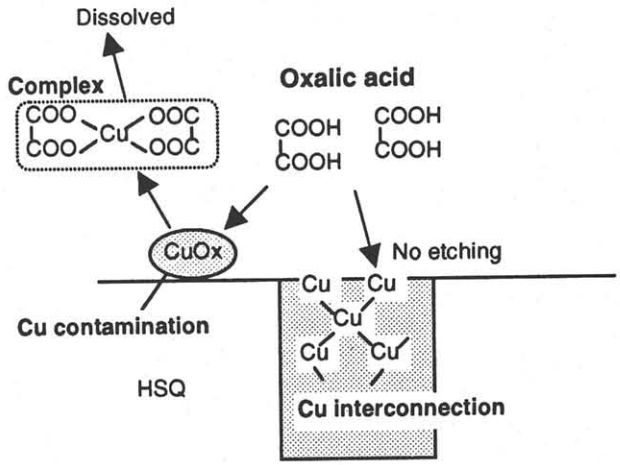

Fig. 5. Mechanism of Cu contamination removal by using oxalic acid without etching the Cu interconnection.

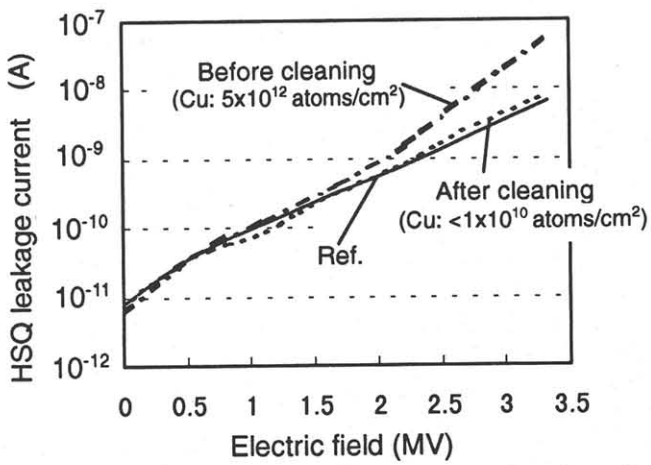

Fig. 6 Leakage current of HSQ films as a function of electric field after 400℃ annealing for 30min.