

Novel Cleaning Solutions for Polysilicon Film Post Chemical Mechanical Polishing

Tung Ming Pan, Tan Fu Lei, *Member, IEEE*, Chao Chyi Chen, Tien Sheng Chao, *Member, IEEE*, Ming Chi Liaw, Wen Lu Yang, Ming Shih Tsai, C. P. Lu, and W. H. Chang

Abstract—Novel cleaning solutions were developed for post-CMP process, surfactant tetra methyl ammonium hydroxide (TMAH) and/or chelating agent ethylene diamine tetra acetic acid (EDTA) were added into the diluted ammonium hydroxide ($\text{NH}_4\text{OH}+\text{H}_2\text{O}$) alkaline aqueous solution to enhance removal of metallic and organic contamination. From the experimental result, it is found that the particle and metal removal efficiency and the electrical characteristics are significantly improved for post-CMP cleaning.

Index Terms—Cleaning, CMP, EDTA, polysilicon, TMAH.

I. INTRODUCTION

CHEMICAL mechanical polishing (CMP) process has become the mainstream planarization technique in the fabrication of deep submicron integrated circuits [1]. As the dimension scales down, the requirement for a cleaner surface after the CMP process becomes more stringent than ever before. There are two major problems. One is the particle, and the other is the metallic impurity contamination on the wafer surface. Brush scrubbing technology has been employed for many years and considered to be the most effective method for removing particles after the CMP process [2]. In terms of the cleaning solutions, the most effective way to remove particles is to use diluted ammonium hydroxide ($\text{NH}_4\text{OH}+\text{H}_2\text{O}$) alkaline aqueous solution which causes the etching of the wafer surface and electrical repulsion to remove the particles.

In this work, the surfactant tetra methyl ammonium hydroxide (TMAH) is used to enhance the particle removal efficiency and the chelating agent ethylene diamine tetra acetic acid (EDTA) is used to reduce the metallic impurity contamination. We found that the particle, the metal removal efficiency and the electrical characteristic can all be improved significantly by using this novel solution.

Manuscript received August 15, 1999; revised January 17, 2000. This work was supported by the joint project of National Nano Device Laboratories and Merck-Kanto Advanced Chemicals Ltd. under Contract C86140. The review of this letter was arranged by Editor T.-J. King.

T. M. Pan and T. F. Lei are with the Department of Electronics Engineering and Institute of Electronics, National Chiao-Tung University, Hsinchu 300, Taiwan, R.O.C.

T. S. Chao, M. C. Liaw, and M. S. Tsai are with the National Nano Device Laboratories, Hsinchu, Taiwan, R.O.C.

C. C. Chen and W. L. Yang are with the Graduate Institute and Department of Electrical Engineering, Feng Chia University, Taichung, Taiwan, R. O. C.

C. P. Lu and W. H. Chang are with Merck-Kanto, Advanced Chemicals Ltd., Taoyuan, Taiwan, R.O.C.

Publisher Item Identifier S 0741-3106(00)04636-X.

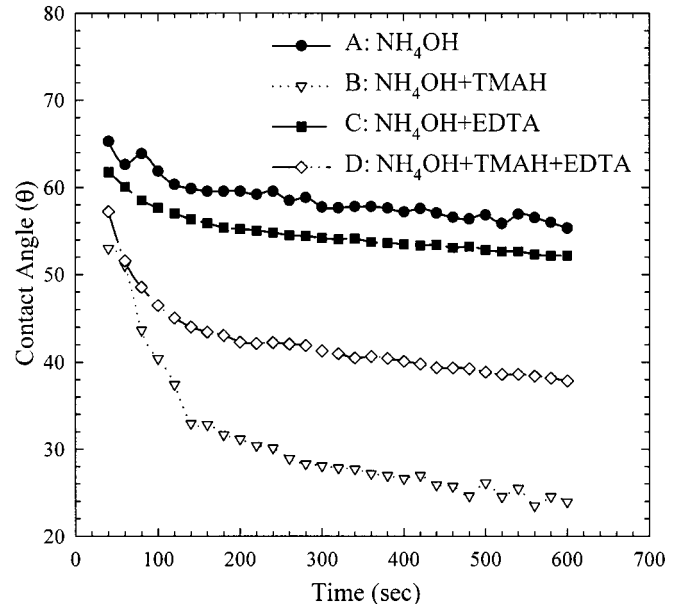


Fig. 1. Depicts the wettability of silicon surface in the contact angle measurement.

II. EXPERIMENTAL

III. RESULTS AND DISCUSSION

Fig. 1 illustrates the wettability of silicon surface in the contact angle measurement. A 300-nm low-pressure chemical-vapor-deposition (LPCVD) doped poly-Si was deposited on an oxide of 4000 Å which was first grown 6-in wafers. The poly-Si CMP experiments were performed on a Westech 372M polisher with diluted CABOT SC-1 slurry. A 500 Å poly-Si was removed during CMP process. After CMP process, wafers were sprayed with diluted NH_4OH solution with megasonic, followed by dispensing the cleaning solution with PVA brush. Different cleaning solutions are (A) diluted 29% NH_4OH , (B) 29% $\text{NH}_4\text{OH} + 2.38\%$ TMAH (volume ratio to NH_4OH is 1%), (C) 29% $\text{NH}_4\text{OH} + \text{EDTA}$ (100 ppm), and (D) 29% $\text{NH}_4\text{OH} + 2.38\%$ TMAH (1%) + EDTA (100 ppm). Poly-oxide capacitors were fabricated to identify the cleaning efficiency after a poly-Si CMP process. In the contact angle measurement, these solutions were dropped on the bare silicon surface after HF solution was dipped to remove native oxide. Particle number was counted by the Tencor surfscan 4500 system. In order to measure metallic impurity concentration absorbed on the poly-Si surface, wafers were dipped in the $\text{Fe}(\text{NO}_3)_3$ slurry solution. The total reflection x-ray fluorescence spectrometry (TXRF) provides a good measure of the metallic impurity.

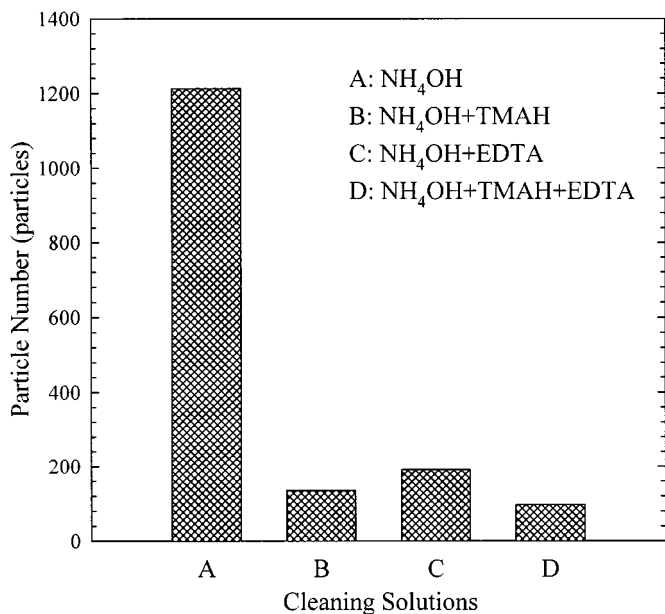


Fig. 2. Particles numbers left on the poly-Si surface after post-CMP cleaning for different solutions.

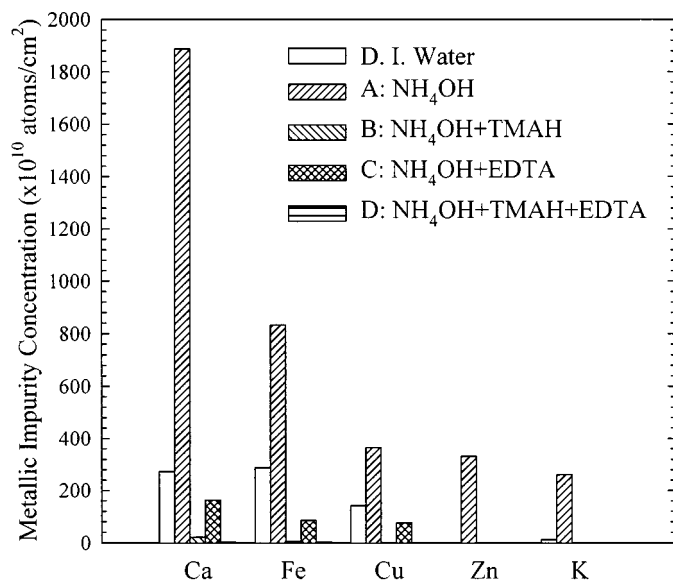


Fig. 3. The metallic contaminant density on poly-Si surface after post-CMP cleaning for different solutions.

The electrical properties of the poly-oxide of the J-E and time dependent dielectric breakdown (TDDB) characteristics were measured by using the Hewlett-Packard (HP) 4145B semiconductor parameter analyzer. It is observed that solution A shows degree of hydrophobicity (high contact angle) and solution B shows degree of hydrophilicity (low contact angle). The reason is that tetra alkyl ammonium cations absorbed on the hydrophobic Si-H surface via van der Waals force. Fig. 2 shows numbers of particles left on the poly-Si surface after post-CMP cleaning for different solutions. It is found that solution A exhibits the lowest efficiency. Both solutions B and C improve the particle removal efficiency significantly. The slight surface etching of the wafer and electrical repulsion between wafer surface and particle can enhance removal of particles. It

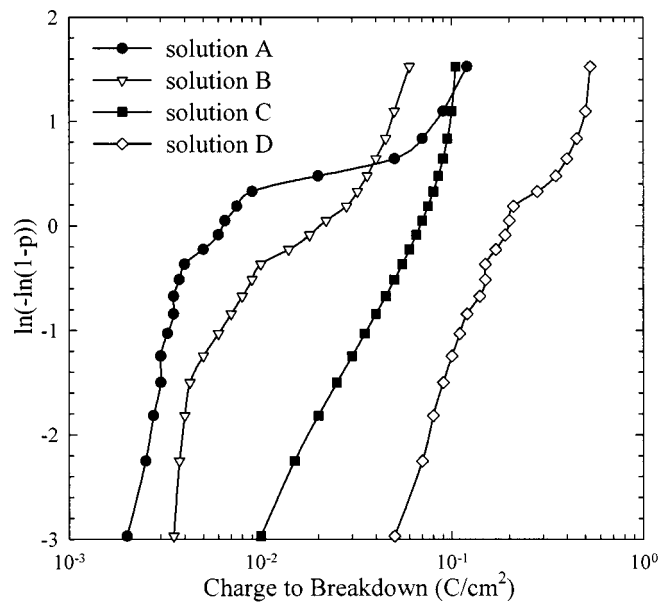


Fig. 4. Charge-to-breakdown distribution of capacitors under constant current stressing after the post-CMP cleaning for four different solutions.

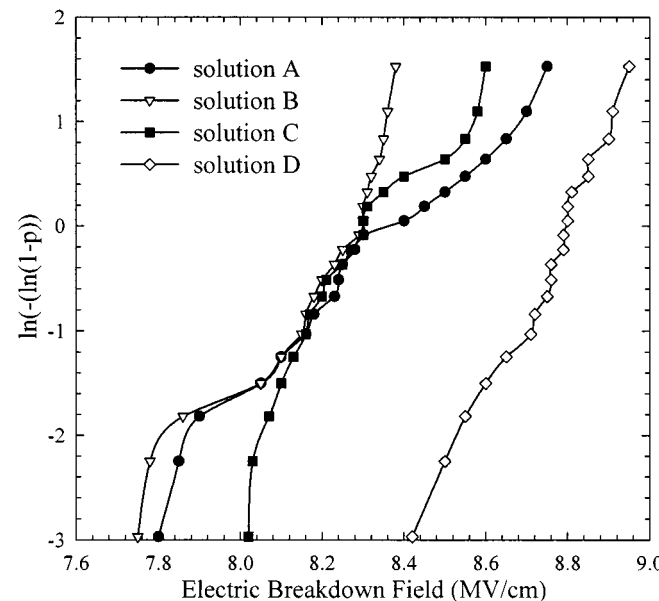


Fig. 5. Breakdown field distribution of capacitors after post-CMP cleaning for four different solutions.

has been shown that hydrophobic surface resides more heavily particles on the wafer surface than hydrophilic surface [3]. From the result of contact angle measurement, TMAH clearly acts as a surfactant that can change the surface property of poly-Si from hydrophobic [4] to hydrophilic. EDTA, on the other hand, can trap the potassium ions, which come from the KOH-base slurry, to reduce solution ionic strength and enhance the electric double layer repulsion between particle and wafer surface [5]. From these data, it seems that both TMAH and EDTA play important roles of particles removal. Combination of TMAH and EDTA results in the best efficiency. Fig. 3 shows the metallic impurity concentrations measured by TXRF. It is very clear that the metallic contaminants are

removed significantly by using the novel solutions, especially for the removal of Ca and Fe ions. The stability constant of metal-EDTA complex depended on pH value [6]. The chelating agent reacts with Fe ion in solution to form Fe-chelate complex [7]. This reaction prevents Fe from getting absorbed poly-Si surface in a form ion hydroxide. Combination of TMAH and EDTA results in the best efficiency.

To investigate the poly-oxide reliability, charge-to-breakdown (Q_{bd}) measurements were performed on capacitors. In Fig. 4 the Weibull distributions are shown under negative bias, i.e., electron injection from the poly-Si-II. The distribution for solution D shows a higher Q_{bd} that can be attributed to efficient removal of particle and metal contaminants on the poly-oxide. The breakdown field distribution is shown in Fig. 5. It is obvious that solution D depicts the largest value among four solutions due to its best performance on reduction of particles and the metal contaminants on the poly-Si surface.

IV. CONCLUSION

In this letter, novel solutions have been demonstrated for post-CMP cleaning. By adding the surfactant (TMAH) and

chelating agent (EDTA) into the diluted ammonium hydroxide ($\text{NH}_4\text{OH}+\text{H}_2\text{O}$) alkaline aqueous solution, removal efficiency of particles and metal impurities is significantly increased, which improves the electrical performances of capacitors in return.

REFERENCES

- [1] G. Bai *et al.*, "Copper interconnection deposition techniques and integration," in *Proc. 1996 Symp. VLSI Technology Dig. Tech. Papers*, 1996, pp. 48–49.
- [2] D. Hymes, I. Malik, J. Zhang, and R. Emami, "Brush scrubbing emerges as future wafer-cleaning technology," *Solid-State Technol.*, pp. 209–214, July 1997.
- [3] W. Kern, *Handbook of Semiconductor Wafer Cleaning Technology*. Park Ridge, NJ: Noyes, 1993, p. 152.
- [4] G. J. Pietsch, Y. H. Chabal, and G. S. Higashi, "Infrared-absorption spectroscopy of Si (100) and Si (111) surface after chemical mechanical polishing," *J. Appl. Phys.*, vol. 78, pp. 1650–1658, 1995.
- [5] J. M. Steigerwald, S. P. Murarka, and R. J. Gutmann, *Chemical Mechanical Planarization of Microelectronic Materials*, New York: Wiley, 1997, p. 294.
- [6] A. Ringbom, *Complexation in Analytical Chemistry*, New York: Wiley, 1963, ch. 2, p. 52.
- [7] H. Morinaga *et al.*, "Advanced alkali cleaning solution for simplification of semiconductor cleaning process," in *Proc. Materials Research Soc. Symp.*, 1997, p. 35.