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# Electrochemical Etching of Ru Film for Bevel Cleaning of BEOL

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## Abstract

We have developed a new wet technology using electrochemical etching for removing Ru (ruthenium) film on the wafer bevel. The etching rate of 50nm/min for Ru film is achieved by diluted HCl solution of less than 0.5%. This process can provide a stable, a low cost and an environmentally friendly process without conventional special and conc. solutions.

## Introduction

A diffusion barrier liner in the Cu/Low-k interconnection is one of the major subjects for 45 nm node devices and beyond. The barrier metal with high diffusion protection by thickness of less than 5nm is required. Ru film as a barrier material instead of conventional TaN film has been investigated [1]. The Ru deposition technique with high coverage for a shallow damascene trench results in the deposition of a film of Ru on the bevel of a wafer. Ru cross-contamination causes damage to the devices on the production line [2]. To prevent cross-contamination, the Ru film must be eliminated from the bevels/edges, and front side-edge exclusion zone (Fig. 1).

However, the Ru film cannot be etched by conventional acidic solutions such as SPM, HPM, or conc. HF to etch Ru film, and even aqua regia has no effect. (see Table 1) Some solutions for Ru etching were reported, chlorine water, cerium(iv) ammonium nitrate, periodic acid, sodium hypochlorite (NaClO), as shown in Table 1. Although these special solutions have some problems such as containing metal in the solution, expensive and unstable reaction.

In this paper, we report on the high performance, of the removal technology of Ru film on the wafer bevel using electrochemical etching.

## Experiment

Fig.2 shows a schematic drawing of bevel etching system using electrochemical method. Both anode and cathode electrodes are inserted in PVA (polyvinyl alcohol) brush. Both brushes contact simultaneously with the wafer bevel. Etching chemical is periodically dropped on both brushes. All around bevel of the wafer can be contacted with both brushes by wafer rotation. Ru film contacted with cathode brush can be etched by electrochemical reaction.

Fig.3 shows an experimental sample for electrochemical etching of Ru film. Ru (thickness: 20nm) / SiO2(thickness :100nm) / Si with 30mm width was used. Chemical (HCl) was dropped on the PVA sponge with carbon electrode. The rate of chemical dropping is 20μL/10sec. Ru film of cathode side was etched by DC supplying.

## Results and discussion

Fig.4 shows the dependence of Ru etching rate on DC supply voltage. The Ru film is etched by supplying DC voltage of more than 2.5V. The supplying voltage is fixed at 4V to keep a stable etching. After Ru etching, $SiO_2$ layer is exposed as shown in Fig.5.

Fig.6 shows the dependence of Ru etching rate on HCl concentration. The Ru etching rate lineally increases for HCl solution with more than 0.1wt.%. The Ru etching rate by 0.5% HCl solution is approximately 50nm/min at room temperature. The etching rate is high enough to remove Ru film of 2-5nm thickness on wafer bevel for 32nm device and beyond.

Fig.7 shows the XPS depth profile of concentration ratio in the Ru film after electrochemical etching by HCl solution. It was found that the surface of Ru film is oxidized after treatment. Cl is detected on the top surface of Ru film. The chemical shifts by Ru-O and Ru-Cl were not clearly observed from the XPS spectra.

Fig.8 shows the electrochemical etching rate of Ru film by various solution. Ru film can be etched by not only acid solution such as HCl, $H_2SO_4$, $HNO_3$, but also alkaline solution such as $NH_4OH$. The etching rate of Ru film by HCl solution is the highest rate in the various solution (1wt.%). It is thought that the Ru film may be easily dissolved through ruthenium oxide or ruthenium hydroxide by supporting electropotential.

## Conclusion

We have succeeded in removing Ru film with high etching rate by using electrochemical etching. The new wet process has been successfully applicable to Ru film removal from the wafer bevel without conventional special and conc. solutions and is a significant step towards the manufacture of next-generation devices.

## Acknowledgements

Thanks to Canon ANELVA Corp. for having the supply of Ru wafer.

## References

[1] S. M. Rossnagel, R. Wisnieff, D. Edelstein, and T. S. Kuan: IEDM Tech. Dig. 83 (2005).

[2] H.Aoki et.al., Ext. Abs. of Int Conf on Solid State Devices & Materials (SSDM), 20 (2001).

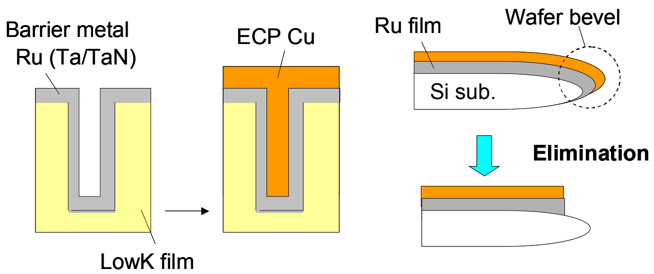


Fig.1. Elimination of Ru film on the wafer bevel for Cu/Low-K process.

Table.1. Etching performance of Ru film for various solutions

| *Solution* | *Ru Etching* | *Problems* |
|---|---|---|
| SPM | No etching | |
| HPM | No etching | |
| Conc.$H_2SO_4$ | No etching | |
| Conc.$HNO_3$ | No etching | |
| Conc.HF | No etching | |
| Aqua regia | No etching | |
| Chlorine water | Etching | Unstable |
| Cerium(iv) ammonium nitrate 〔$(Ce(NH_4)_2Ce(NO_3)_6$〕 | Etching | Containing metal (Ce) |
| Periodic acid ($H_5IO_6$) | Etching | Expensive |
| NaClO | Etching | Containing metal (Na) |

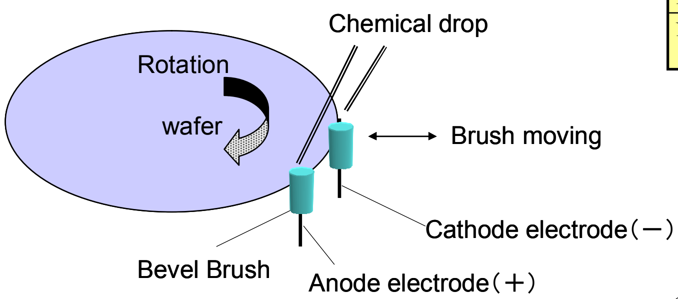


Fig.2. A schematic drawing of bevel etching system using electrochemical method.

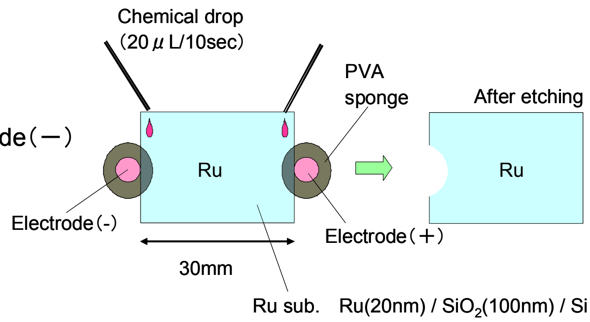


Fig.3. An experimental sample for electrochemical etching of Ru film.

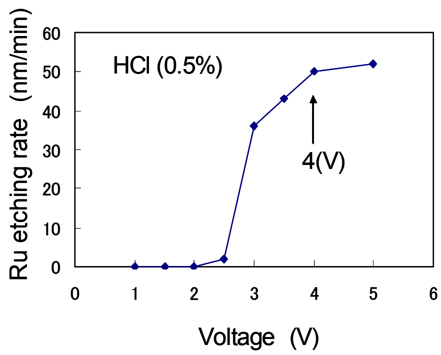


Fig.4 Dependence of Ru etching rate on DC supply voltage.

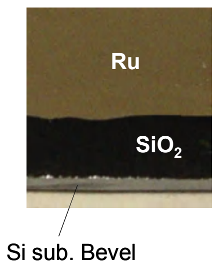


Fig.5 Wafer edge with Ru film after electrochemical etching

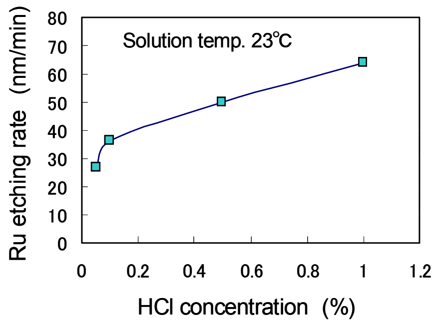


Fig.6. Dependence of Ru etching rate on HCl concentration.

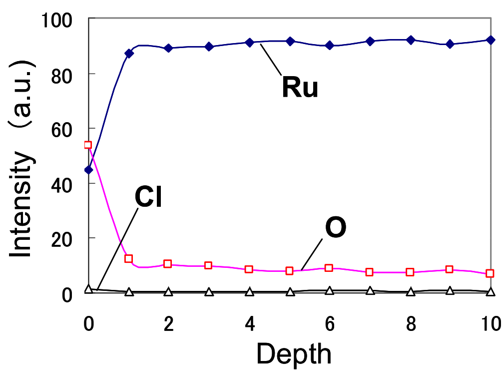


Fig.7. XPS depth profile of concentration ratio in the Ru film after electrochemical etching by HCl solution.

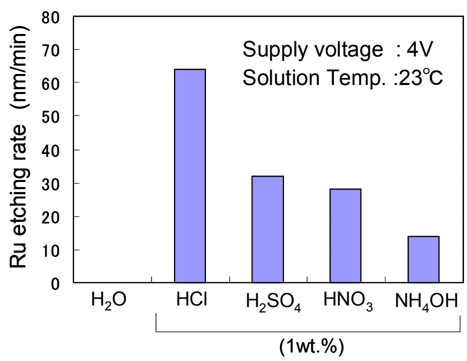


Fig.8. Electrochemical etching rate of Ru film by various solution.