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Ruthenium Film Etching and Cleaning Process Using Cerium Ammonium Nitrate (CAN)-Nitric Acid

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ABSTRACT

We have developed a process in which a mixture of cerium ammonium nitrate (CAN) and nitric acid is used to wet-etch and clean Ru (ruthenium) film. This process provides higher etching rates and a better performance in cleaning at low temperatures than processes based on the application of periodic acid. This solution also achieves a low cost for the process because of its long life and the cheapness of the raw materials required to produce it.

1. INTRODUCTION

Electrodes made of ruthenium (Ru) will be required for use in the capacitors of next-generation devices, such as those of DRAM cells with MIM capacitors in which the dielectric is of Ta₂O₅, (Ba,Sr)TiO₃ [BST], or SrTiO₃[STO]. The CVD of Ru is required to form a capacitor with a high-aspect ratio¹⁾, but results in the deposition of a film of Ru on the backside and/or bevel of a wafer. Ru cross-contamination causes damage to the device on the production line and can thus dramatically shorten the lifetime of the device. To prevent cross-contamination, Ru must be eliminated from the wafer's backside, bevels/edges, and frontside-edge exclusion zone (Fig. 2).

The use of periodic acid (H₅IO₆) to wet-etch Ru film has been reported²⁾. In this paper, we report on the better performance, in the wet-etching and cleaning of Ru film, of a mixture, in solution, of cerium (IV) ammonium nitrate [(Ce(NH₄)₂Ce(NO₃)₆)] and nitric acid.

2. EXPERIMENTAL and RESULTS

Ru contamination dramatically decreases recombination lifetimes as well as platinum levels. This is shown in Figure 3. It is not possible to use a conventional acidic solution that operates by oxidation, such as SPM, HPM, or conc. HF to etch Ru film, and even aqua regia has no effect. (see Table 1) The only agent we found to be effective in etching a film of Ru, other than periodic acid, was a solution of cerium (IV) ammonium nitrate (CAN). The CAN is easily hydrolyzed in an aqueous solution, but this hydrolysis can be suppressed by including nitric acid in the mixture.

The rate at which the Ru film is etched on dipping into the solution described above decreases as the concentration of nitric acid increases. This is shown in Fig. 4. The etching rate was, however, dramatically increased by stirring. The Ru-etching rate during spin treatment (at 200 rpm) was about five times greater than the rate during dipping.

Figure 5 shows the dependences of the rates of etching of (a) Ru film and (b) RuO₂ film on the temperature of treatment by CAN-nitric acid and periodic acid, respectively. The rate of etching of the Ru film by CAN-nitric acid is less strongly dependent on temperature than the rate of etching by periodic acid. CAN-nitric acid is thus able to efficiently etch Ru film at low temperatures.

Figure 5 (b) shows that CAN-nitric acid is able to etch RuO₂-film, while periodic acid is not. This indicates that CAN-nitric acid is able to dissolve Ru contamination even when the Ru contamination is adsorbed onto the wafer in the form of RuO₂.

Figure 6 shows the dependence of the normalized

etching rates on the number of treated wafers. This was estimated from the dissolved volume of Ru film. The rate of etching by CAN-nitric acid changes little, even after the etching of a lot of Ru films. However, the rate of etching by periodic acid decreases quite sharply as the volume of dissolved Ru in the solution increases.

Figure 7 is an SEM photograph of a wafer's frontside edge after treatment by a wraparound spin cleaner³⁾. The effective elimination of Ru film on the wafer's bevel/edge and a 2.5-mm frontside-edge exclusion zone was achieved. Figure 8 shows the level of metallic contamination on a sample wafer's backside before/after a two-stage cleaning process. Cleaning in a CAN (20%)-nitric acid (10%) solution was followed by HF-based acid cleaning. Ce contamination remained on the wafer after cleaning in the solution of CAN-nitric acid. This is, of course, because of the Ce contained in the solution. Fortunately, HF-based-acid cleaning was able to easily remove the Ce. Ru contamination is reduced to a level of <10¹⁰ atoms/cm² after this cleaning sequence. Contamination by other metals, such as Cu, Fe, and Ce, was also reduced to <1x10¹⁰ atoms/cm².

3. DISCUSSION

We have determined what we believe to be the mechanism for the dissolution of Ru film by cerium ammonium nitrate-nitric acid solution. This is shown in Fig. 9. Noble metals, like Ru, can be made soluble by oxidation. Cerium (IV) is a good oxidizer of ruthenium and reduces itself to cerium (III). Ru is oxidized by cerium (IV) in two steps. Firstly, Ru is oxidized to ruthenium hydroxide (Ru(OH)₃ or Ru(OH)₄). An acidic solution is then able to dissolve ruthenium hydroxide. This allows the etching of Ru film by a solution of CAN-nitric acid. Ruthenium hydroxide is oxidized continuously to produce RuO₄. As this is a volatile compound, the Ru rapidly leaves the solution of CAN-nitric acid. Little of the dissolved Ru remains in the solution of CAN-nitric acid, so Ru cross-contamination of the next wafer is suppressed when the used solution must be recycled. The etching performance of the solution also exhibits little change with use as is shown in Figure 7. These qualities, along with the cheapness of the raw materials required to produce the solution, make it very attractive.

4. CONCLUSIONS

A new wet process using a solution of cerium ammonium nitrate and nitric acid has been successfully applied in removing the Ru film and residual Ru contamination from the backsides of wafers. The Ru wet-etching/cleaning process that we have described, with its high performance and low cost, is a significant step towards the manufacture of next-generation devices that will feature Ru electrodes.

References

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- [2] T. Saeki et. al., Extended Abstracts (The 48th Spring Meeting 2001), The Japan Society of Applied. Phys. and Related Soc., p.830 (2001).
- [3] P.S. Lysaght et al., Proc. of ECS, 99-36, p. 343 (1999).

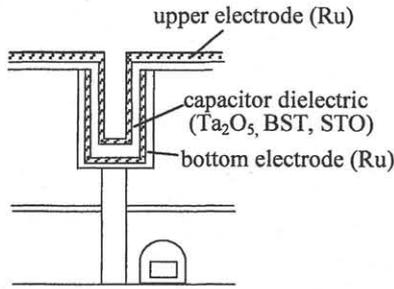


Fig. 1 Typical capacitor structure using an Ru electrode.

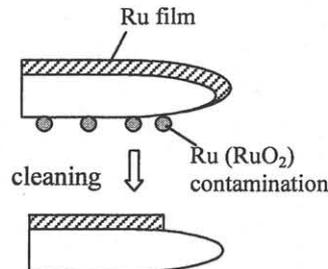


Fig. 2 Ru film and Ru contamination on the wafer.

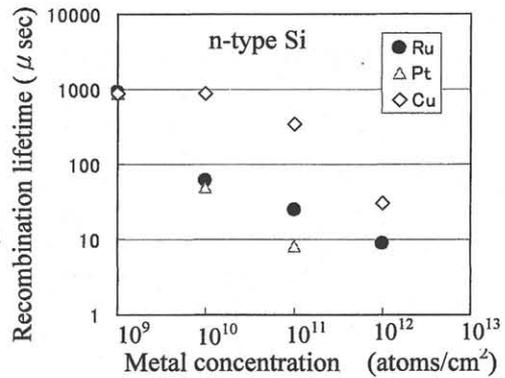


Fig. 3 Dependence of recombination lifetime on metal (Ru, Pt, Cu) concentration.

Table 1 Ru film etching rate when dipping in various acids.

Solution (treatment temp.)	Etching rate
SPM [H ₂ SO ₄ /H ₂ O ₂] (120°C)	No etching
HPM [HCl/H ₂ O ₂ /H ₂ O] (80°C)	No etching
Conc. H ₂ SO ₄ (120°C)	No etching
Conc. HNO ₃ (80°C)	No etching
Conc. HF (80°C)	No etching
Aqua regia (80°C)	No etching
Iron (III) Nitrate (60°C)	No etching
Sodium bromate (60°C)	No etching
Potassium permanganate (60°C)	No etching
Cerium (iv) ammonium nitrate [CAN] (60°C)	90 nm/min
periodic acid (60°C)	92 nm/min

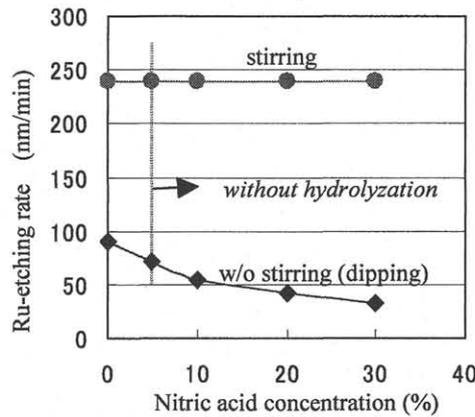


Fig. 4 Ru film etching rate vs nitric acid concentration for dipping and stirring in a solution of CAN-nitric acid (at 60°C).

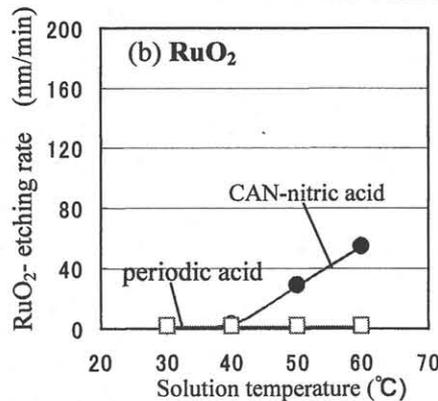
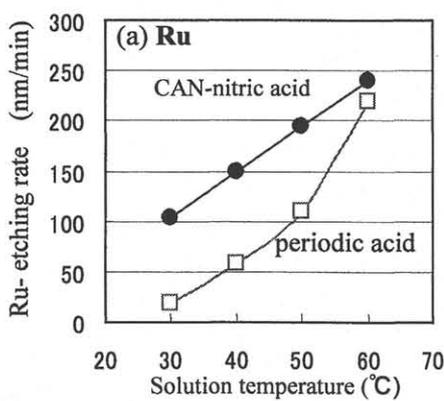


Fig. 5 Dependence of rates of etching (a) Ru film and (b) RuO₂ film on solution temperature.

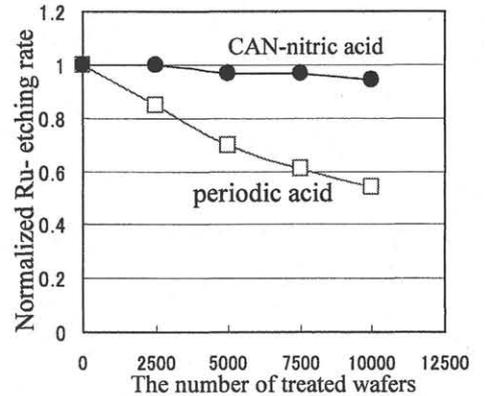


Fig. 6 Normalized Ru-film etching rates according to the estimated number of treated wafers. (8 inch wafer edge-cut 2mm)

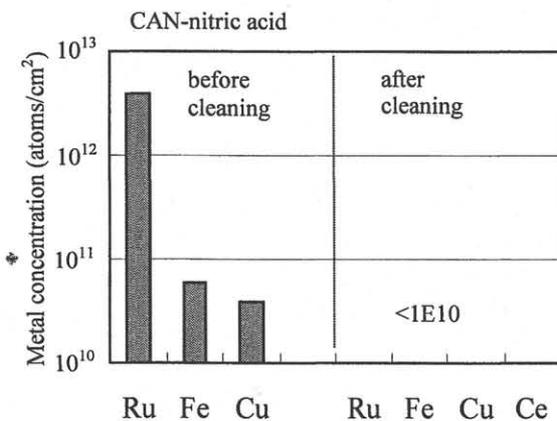


Fig. 8 Metallic contamination levels on a wafer backside before/after cleaning using the CAN-nitric acid solution then HF-based acid cleaning.

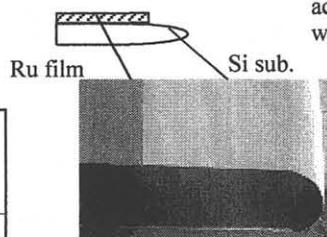


Fig. 7 Eliminating Ru film on wafer bevels/edges and the frontside edge exclusion zone (2.5 mm).

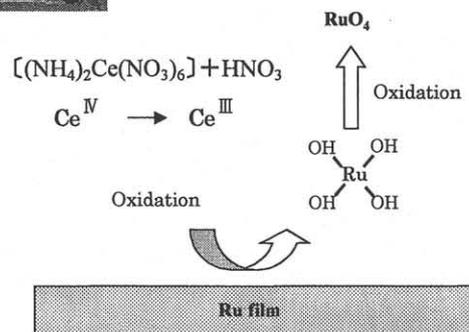


Fig. 9 Mechanism by which the CAN-nitric acid solution etches Ru film.