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Ru CMP 공정에서의 화학액과 연마 입자 농도에 따른 연마율과 표면 특성

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Effects of Chemical and Abrasive Particles for the Removal Rate and Surface Microroughness in Ruthenium CMP

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Abstract

MIM capacitor has been investigated for the next generation DRAM. Conventional poly-Si bottom electrode cannot satisfy the requirement of electrical properties and comparability to the high k materials. New bottom electrode material such as ruthenium has been suggested in the fabrication of MIM structure capacitor. However, the ruthenium has to be planarized due to the backend scalability. For the planarization CMP has been widely used in the manufacture of integrated circuit.

In this research, ruthenium thin film was polished by CMP with cerium ammonium nitrate (CAN)base slurry. HNO3 was added on the CAN solution as an additive. In the various concentration of chemical and alumina abrasive, ruthenium surface was etched and polished. After static etching and polishing, etching and removal rate was investigated. Also microroughness of surface was observed by AFM. The etching and removal rate depended on the concentration of CAN, and HNO3 accelerated the etching and polishing of ruthenium. The reasonable removal rate and microroughness of surface was achieved in the 1wt% alumina slurry.

Key Words : CMP, Ruthenium, Removal Rate, Microroughness

1. Introduction

In the future DRAM technology, capacitor which has the metal bottom electrode, has been suggested to maintain the capacitance in shrinking cell size [1-2]. Recently, Ta_2O_5 or $(Ba,Sr)TiO_3$(BST) has been discussed to the dielectric materials for high capacitance because of their high dielectric constant [3]. However, the conventional capacitor has the semiconductor bottom electrode which is called MIS (Metal-Insulator-Semiconductor) capacitor compared with the metal bottom electrode capacitor (MIM capacitor). Among the novel metal, ruthenium is a candidate for the bottom electrode metal because of the excellent electrical performance, a low leakage of current, and the comparability to the high dielectric constant material [4].

However, there are several issues in the application of these novel metals for MIM structure capacitor. One of them is the difficulty of planarizing the steps of cylinder capacitor to meet the requirement of the backend scalability. Therefore the maskless polishing technology or chemical mechanical planarization (CMP) was introduced to remove the bottom electrode [5]. Recently, Bilakhiya et al. [6] have employed a

cerium ammonium nitrate $[(NH_4)_2Ce(NO_3)_6]$ (CAN) solution dissolved in HNO_3 in order to oxidize Ru with cerium (Ⅳ) (Ce^{4+}) ions. In the previous research, it was found that the Ru thin film was etched and polished by CAN chemistry [7].

In this study, the removal and etch rate of Ru thin film was investigated in the various concentration of CAN. Also the surfaces were analyzed by atomic force microscopy (AFM) after etching and CMP.

2. Experimental

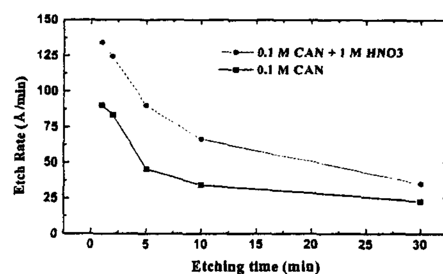
Ru thin film(~1200Å) was deposited by puttering on 550Å TiN/Ti barrier layer. This blanket wafers were cut into 2×2 cm for polishing and static etching experiments. Cerium ammonium nitrate (CAN; $(NH_4)_2Ce(NO_3)_6$) was applied to etch ruthenium surface and HNO_3 was used for additive. Ruthenium deposited wafers were immersed into 0.1M CAN solution and the mixing solution of 0.1M CAN and 1M HNO_3, respectively.

CMP experiments were carried out with Logitech PM5 polisher and Rodel IC1400 k-groove pad. Alumina particle (99.99 wt%, primary size <50nm) was purchased from Degussa Co. and used to abrasive particles. In order to make the slurry, zirconia (ZrO_2) bead was added to the chemical solution including alumina abrasive particles and the chemical solution was shaken during 30 min. The carrier and platen speed was set at 50 rpm. The down pressure of carrier was 6.5 psi and slurry flow rate was constant to 110ml/min during 1 min polishing.

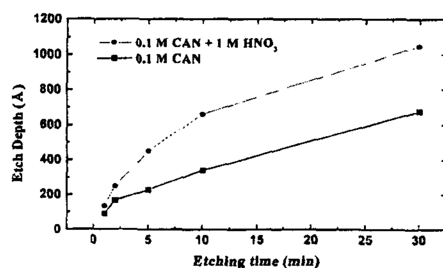
After etching and polishing, the wafer surfaces were rinsed with DI water and then dried by N_2 blowing. DI water (18.2 MΩcm) was used for all the static etching, slurry preparation and rinsing. The removal and etch rate of ruthenium were measured by using a four-point probe (Chang Min Tech Co. Ltd, CMT-SR1000N). The etched and polished wafer surfaces were observed by AFM (AutoProbe CP Research, PSIA Co.). Particle size was measured by LEZA-600 (Otsuka Electronics Co.).

3. Results and Discussion

Figure 1 shows the results of static etching as a function of etching time. All etchings were carried out in the room temperature. After 1 min etching, the etched thickness was about 90Å in the 0.1M CAN solution and 134Å in the 0.1M CAN and 1M HNO_3 solution, respectively. The etch rate decreased as the etching time increased in the both etching solution with and without HNO_3. However the total etched thickness of ruthenium thin film increased linearly. In the HNO_3 added etching solution, the etch rate and etched thickness was higher than in the only CAN solution. This means that the HNO_3 accelerated the etching of ruthenium in the CAN solution.



(a)



(b)

Fig. 1. (a) Static etch rate and (b) etch depth as a function of etching time in 0.1M CAN and 1M HNO_3 solution

After static etching, the ruthenium surface was observed by AFM. The spherical shape products

were existed on the surfaces as shown in Fig. 2. Microroughness of etched surfaces was from 6nm to 7.5nm.

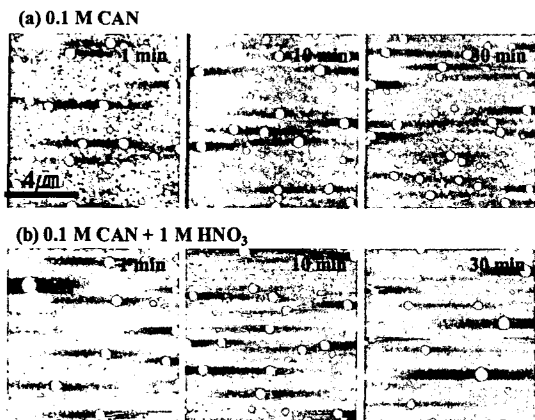


Fig. 2. AFM images of ruthenium surface after static etching in (a) 0.1M CAN and (b) 0.1M CAN and 1M HNO_3 solution

Ruthenium thin film was etched during 1 min in the various concentration of CAN with and without 1M HNO_3. The etched thickness increased linearly as the concentration of CAN increase as shown in Fig. 3. Although the etched thickness of ruthenium thin film was higher in the HNO_3 added etching solution, ruthenium was etched very slightly in the 0.01M CAN etching solution regardless of existing of HNO_3.

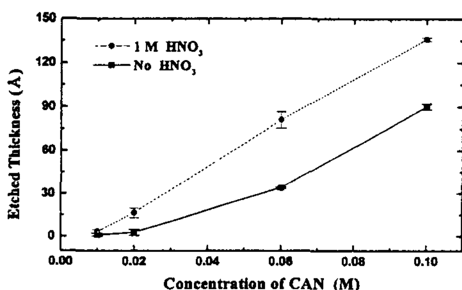


Fig. 3. Etched thickness in the various concentration of CAN with and without HNO_3

Figure 4 shows the removal rate of ruthenium in the 1 wt% alumina added slurry. In the slurry without HNO_3, the removal rate had the same tendency with etch rate. However, the removal rate was over 1000 in the HNO_3 added slurry except the slurry of 0.01M CAN. Although the ruthenium was polished completely in the 0.06 and 0.1M CAN slurry including HNO_3, the removal rate was very low in the 0.01 and 0.02M concentration of CAN slurry.

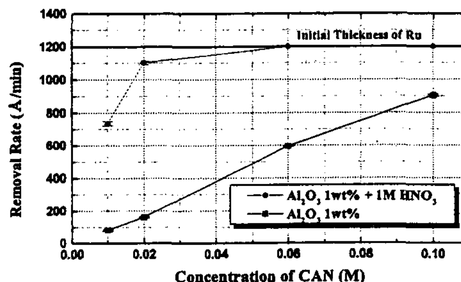


Fig. 4. Removal rate of ruthenium in 1wt% alumina added slurries

The high removal rate in the HNO_3 added slurry is due to the agglomerated abrasive particles as shown in Fig. 5. When the HNO_3 added to the CAN solution, the alumina particles size was over 900nm and four or five times bigger than that of only CAN solution. And stability of alumina particles was poor.

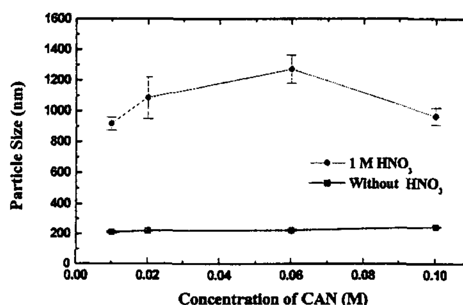


Fig. 5. Particle size of alumina abrasive in CAN solution with and without 1M HNO_3

At the chemical composition of 0.1M CAN with and without 1M HNO_3, the concentration of alumina particles was changed. Figure 6 shows the results of removal rate as a function of concentration of alumina abrasives. The removal

rate was 400Å/min in the 0.1M CAN chemical solution without abrasives. This result shows that the ruthenium thin film could be polished by only chemical solution and direct friction between the ruthenium and pad surfaces. The removal rate increased to 830Å/min in the 1M HNO_3 added solution and this removal rate was rather higher than in the slurry composed of 1 wt% alumina abrasive and 0.01, 0.02 and 0.06M CAN solution. Therefore, it was fact that the addition of HNO_3 influenced greatly the increasing of removal rate. In the 0.1M CAN slurry without HNO_3, the removal rate was saturated at the concentration of 1 wt% alumina and didn't increase at the 2 and 5 wt% alumina slurry. However, the ruthenium was removed completely when 1M HNO_3 and alumina abrasive added on the 0.1M CAN.

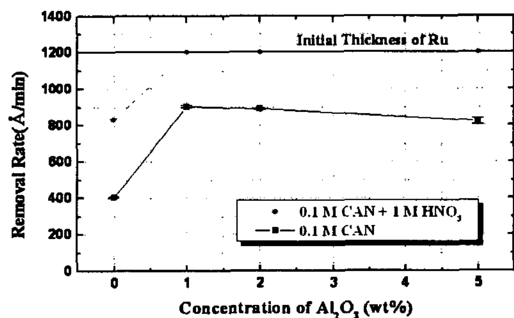


Fig. 6. Removal rate in the various concentration of alumina abrasive

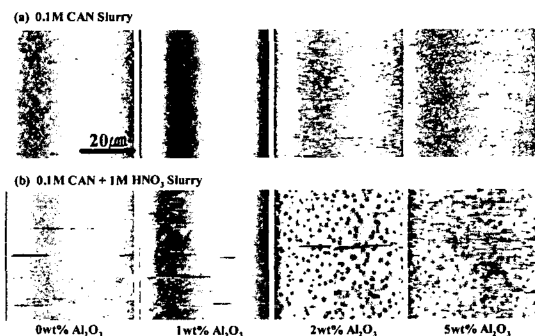


Fig. 7. Polished surfaces of ruthenium after CMP in (a) 0.1M CAN and (b) 0.1M CAN+1M HNO_3 slurry

After polishing, ruthenium surfaces were observed by AFM. Figure 7 shows the polished ruthenium surfaces in the various slurries. Products were existed on the surface which was polished with the abrasive free 0.1M CAN slurry as same as the products were observed on the etched surfaces. Magnitude of microroughness was lowest in the 1wt% alumina slurry.

Because of the chemical effect, the microroughness increased in the abrasive free slurries. Also the microroughness of ruthenium surfaces increased when the surface was polished by 2 and 5 wt% alumina slurries.

4.Summary

The static etching of ruthenium surface was dependent on the concentration of CAN (Cerium Ammonium Nitrate). And HNO_3 accelerated the static etching. In the various concentration of CAN without HNO_3, the removal rate increased linearly like the static etching. The high removal rate was achieved in the HNO_3 added slurry due to the agglomerated alumina particles. Stability of HNO_3 added slurry was poor and the abrasive particle size was larger than that of only CAN slurry. High removal rate and low microroughness was achieved at 1 wt% alumina slurry.

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