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High-rate Ru electrode etching using O_2/Cl_2 inductively coupled plasma

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Abstract

We have studied the characteristics of Ru etching using O_2/Cl_2 plasmas in an inductively coupled plasma (ICP) etcher. The changes of Ru etch rates and Ru electrode etching slopes by varying $Cl_2/(O_2 + Cl_2)$ gas flow ratio, total flow rate, source power, bias power, and pressure were investigated. A high Ru etch rate of >1400 Å/min with a high etching slope of $>85°$ was demonstrated using 0.15 μm critical dimension (CD) patterned wafers. The mechanism of high-rate Ru etching is studied.

Keywords: Ru; Etching; ICP; Transmission electron microscopy

1. Introduction

As the dimension of devices decrease in size, high-*k* dielectric materials, such as barium strontium titanate (BST), and tantalum pentoxide (Ta_2O_5), need to be used for the fabrication of dynamic random access memory (DRAM) capacitors [1–4].

Although platinum (Pt) has usually been investigated as an electrode material, Pt had an etching problem. Several research groups have reported that obtaining the sufficient etching selectivity of Pt to the mask material, is very difficult [5–8]. On the other hand, ruthenium (Ru) is expected to be patterned by chemical etching, because the volatile etch product can be produced [9,10].

It is known that RuO_3 and RuO_4 are volatile species in which RuO_4 has relatively low melting and boiling points (25.4 °C and 40 °C, respectively) [10]. The RuO_4 compound should be treated as the

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etching product, because it is the only product which has a much higher vapor pressure. Additive gas including Cl_2 gas is known to increase the etch rate of RuO_2 by increasing the concentration of oxygen radicals [12], and it is surmised that the Cl_xO_x radical as an etchant reacts with RuO_2, forming the volatile RuO_4 [11].

Regarding Ru etching, it is known that Ru changes to RuO_2 and then subsequently changes to RuO_4. However, there are not many systematic studies on the basic characteristics of Ru etching. In this work, we report the etching characteristics of Ru using O_2/Cl_2 inductively coupled plasmas (ICP), because we have surmised that the ICP plasma effectively increased the amount of radicals, which are crucial for efficient Ru etching. We investigate the variation of the Ru etch rate and the Ru etching slope by varying process conditions including pressure, source and bias power, total gas flow rate, and $Cl_2/(O_2 + Cl_2)$ gas flow ratio. A Ru etch rate higher than 1000 Å/min is reported for the first time. The Ru surface after etching is investigated.

2. Experiments

A DPS centura ICP tool commercially available from Applied Materials has been used. During etching, the source power was 1000–2000 W, the bias power was 100–500 W, the pressure was 10–50 mTorr and the total gas flow rate was 100–400 sccm. The cathode temperature was set to 45 °C and the helium pressure was set to 15 Torr.

A storage node pattern with a critical dimension (CD) of 0.15 nm was used in our experiments. The top view of the storage node pattern indicates that the storage node is an oval type, and space CDs along the short axis and the long axis are 150 nm and 250 nm, respectively. The sample structure was Si substrate/TiN 600 Å/Ru 4000 Å/SiO_2 mask 2000 Å. SiO_2 mask, instead of the photoresist mask, was used for patterning Ru, because oxygen gas was the main etchant in our experiments. The SiO_2 mask was patterned by CF_4/N_2/Ar gas.

As Ru cannot be etched by halogen gases due to the high boiling point of their etch products, we used O_2 gas as a main etchant, expecting that the volatile RuO_4 would be produced [9,10]. The Cl_2 gas was added to enhance the etch rate.

A scanning electron microscope (SEM) was used to measure the Ru etching slope and the resulting bottom space between two adjacent nodes after the etching process. The Ru surface after etching was analyzed by transmission electron microscopy (TEM). In order to prepare a sample for SEM and TEM observation, a wafer was cut along the short axis of the storage node patterns.

3. Results and discussion

To investigate the etching characteristics of the Ru electrode using O_2/Cl_2 inductively coupled plasma, the $Cl_2/(O_2 + Cl_2)$ gas flow ratio, total gas flow rate, pressure, source power and bias power were varied. Fig. 1 shows the change of Ru etch rate and etching slope with a varying $Cl_2/(O_2 + Cl_2)$ gas flow ratio in the range of 0.1 to 0.4, revealing that the Ru etch rate of about 1450 Å/min is attained at the $Cl_2/(O_2 + Cl_2)$ gas flow ratio of 0.2. The Ru etching slope increases by increasing the $Cl_2/(O_2 + Cl_2)$ gas flow ratio.

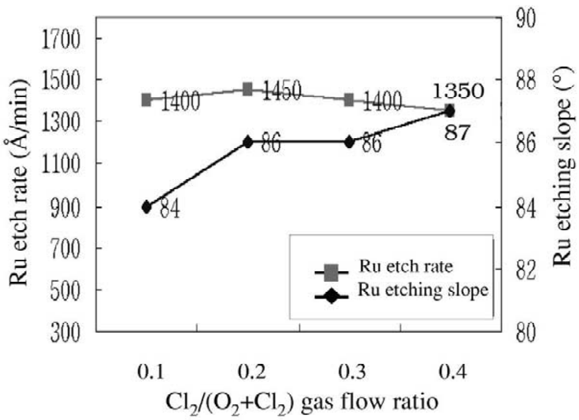


Fig. 1. Variation of Ru etch rate and etching slope by varying $Cl_2/(O_2+Cl_2)$ gas flow ratio.

To investigate the role of Cl_2 in Ru etching, we replace Cl_2 in O_2/Cl_2 plasma with other elements. The total flow rate was fixed to 200 sccm. When the O_2 flow rate is 160 sccm and the Cl_2 flow rate is 40 sccm, the etch rate is measured to be 1370 Å/min. However, when 40 sccm of BCl_3, CHF_3, and SF_6 gas replace 40 sccm of Cl_2 gas, respectively, the Ru etch rates are about 75, 525, and 200 Å/min. When the O_2 flow rate is 200 sccm without any additive gas, the etch rate is measured to be about 200 Å/min. Therefore, it is probable that the Cl_2 gas plays a crucial role in obtaining an efficient Ru etching.

Fig. 2 shows the change in the Ru etch rate and etching slope by varying the total gas flow rate in the range of 100 to 400 sccm, revealing that the Ru etch rate and Ru etching slope increases by increasing the total flow rate. We surmise that the amount of radical flux per unit time may increase and thus, the Ru etching reaction may be enhanced by increasing gas flow rates.

Fig. 3 shows the change of Ru etch rate and etching slope by varying source power in the range of 1200 to 1800 W. The Ru etch rate increases significantly by increasing source power. The etch rate increased by increasing microwave power in RuO_2 etching experiments using electron cyclotron

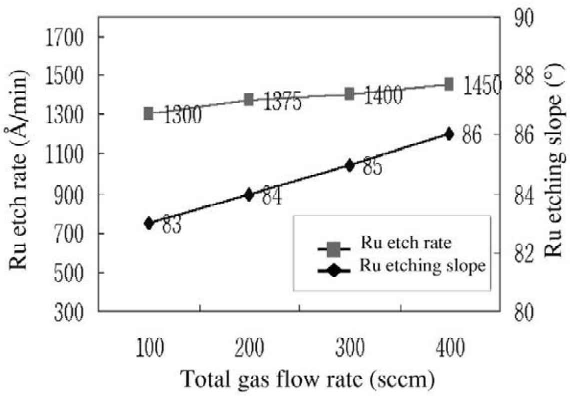


Fig. 2. Variation of Ru etch rate and etching slope by varying total gas flow rate.

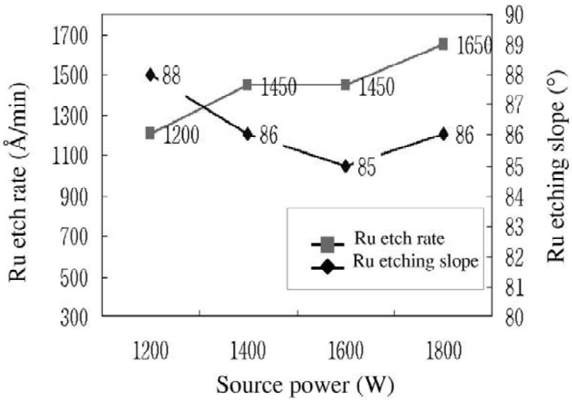


Fig. 3. Variation of Ru etch rate and etching slope by varying source power.

resonance (ECR) plasma [11]. We surmise that the amount of radicals may increase and thus the Ru etching reaction may be enhanced by increasing source power.

Fig. 4 shows the change of Ru etch rate and etching slope by varying bias power in the range of 100 to 400 W. Both the Ru etch rate and etching slope increase by increasing bias power and become saturated at a bias power of 300 W. We surmise that the ion bombardment affects the Ru etching, because the bias power is closely related to ion bombardment energy.

We have investigated the etching characteristics with the change of pressure in the range of 10 to 50 mTorr (Fig. 5). Due to the limitation of our system, the 10–20 mTorr-range experiments and the 20–50 mTorr-range experiments were performed at total gas flow rates of 100 sccm and 400 sccm, respectively. We reveal that the Ru etch rate and Ru etching slope increase with increasing pressure at a low-pressure regime (Fig. 5a). However, Fig. 5b indicates that the Ru etch rate and the etching slope decrease with increasing pressure in the range of 30–50 mTorr.

In the optimized etching condition, which was obtained from our experiments, the total flow rate is 400 sccm (320 sccm O_2/80 sccm Cl_2) and source power is 1400 W, bias power is 200 W, and pressure is 30 mTorr. We used the optimized etching condition. The cross sectional TEM image of a Ru electrode storage node pattern with a CD of 0.15 μm is shown in Fig. 6. An etching slope of 86° is

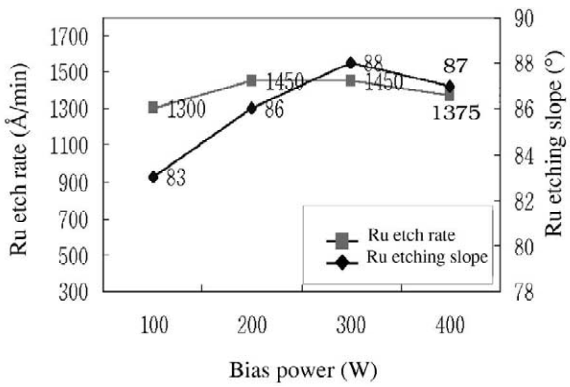


Fig. 4. Variation of Ru etch rate and etching slope by varying bias power.

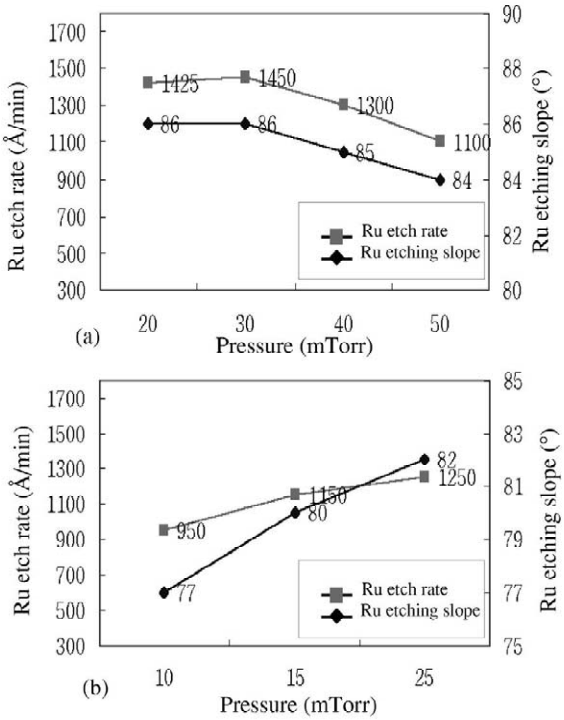


Fig. 5. Variation of Ru etch rate and etching slope by varying pressure (a) at 100 sccm and (b) at 400 sccm.

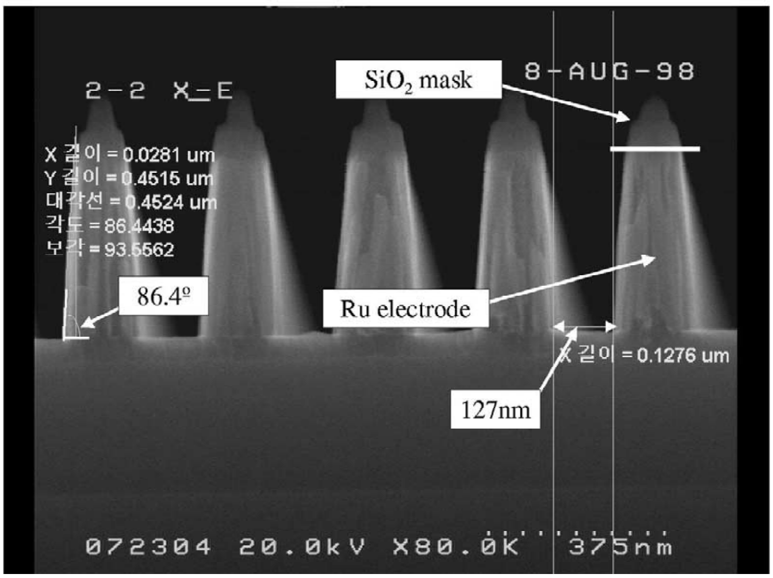
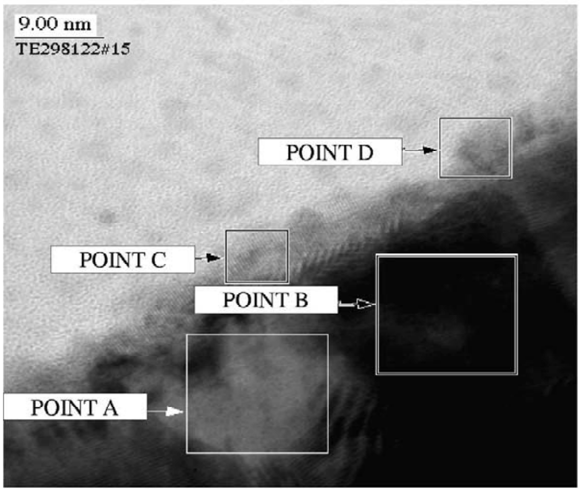


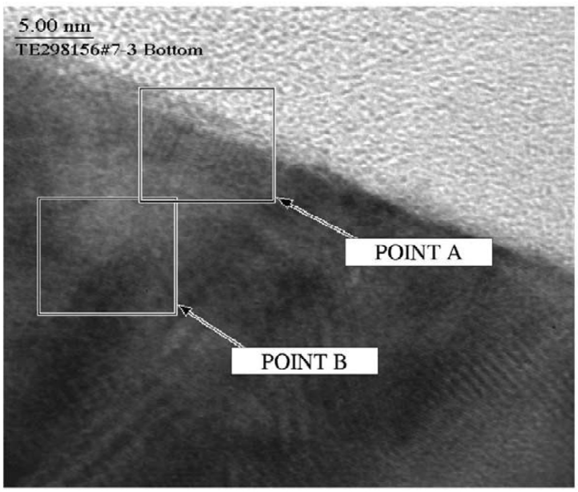
Fig. 6. TEM image of Ru electrode storage node pattern with a CD of 0.15 μm, revealing an etching slope of 86° and the bottom space between two adjacent nodes of about 120 nm. The total flow rate is 400 sccm (320 sccm O_2/80 sccm Cl_2) and source power is 1400 W, bias power is 200 W and pressure is 30 mTorr.

attained and thus, the bottom space between two adjacent nodes is about 120 nm. The following steps of BST deposition (estimated to be $\geq$300 Å in thickness per side) and the top electrode Ru deposition can be accomplished.

To investigate the characteristics of the etched Ru surface, we compared two different samples, which were patterned with two different etching conditions using O_2/Cl_2 plasma. Fig. 7a shows a TEM image of a sample in which the Ru etch rate is very low (about 200 Å/min), revealing that an additional layer is formed on top of the Ru layer. The average thickness of the additional layer is about 70 Å. By obtaining the diffraction pattern and employing the Fourier transformation, the materials at point 'C' and at point 'D' are identified as RuO_2 (Fig. 7a). The distance between two



(a) Etch rate $<$ 300 •/min



(b) Etch rate$>$ 1400 •/min

Fig. 7. TEM image of an etched Ru surface when (b) etch rate is high ($>$1400 Å/min) and when (a) etch rate is low ($<$300 Å/min).

adjacent crystalline planes of the material at position 'C' and 'D' is measured to be 3.2 Å, which corresponds to the lattice parameter of RuO_2 (110). On the other hand, the distance between two adjacent crystalline planes of the material at position 'A' and 'B' is measured to be 2.4 Å, which corresponds to the lattice parameter of Ru(100). Fig. 7b shows a TEM image of a sample in which the Ru etch rate is high (>1400 Å/min), revealing that no RuO_2 is found when the Ru etching occurs efficiently (Fig. 7b).

We surmise that Ru can be changed to RuO_2 and then RuO_2 is changed to volatile RuO_4. The change of RuO_2 to RuO_4 is accelerated by the addition of Cl-species and if this reaction is fast, then the RuO_2 layer will be kept thin. It is confirmed by our high resolution transmission electron microscopy (HRTEM) observation that the RuO_2 layer exists on the Ru surface when the Ru etching does not occur efficiently (Fig. 7a). Therefore in the Ru etching using O_2/Cl_2 ICP, the formation of RuO_4 from RuO_2 is a crucial step. If it does not proceed properly, the RuO_2 layer exists and can be observed. Further study is necessary to disclose the detailed mechanism.

4. Conclusion

A Ru electrode has been etched in inductively coupled plasma O_2/Cl_2 discharges. The variation of Ru etch rate and Ru etching slope by varying process parameters, such as $Cl_2/(O_2 + Cl_2)$ gas flow ratio, total flow rate, source power, bias power, and pressure has been investigated. It is noteworthy that a high etch rate of >1400 Å/min with a high etching slope of $>85°$ was attained using 0.15 μm CD patterned wafers. TEM observation indicates that the Ru surface after etching, with a high etching rate, contains no RuO_x layer, while the Ru surface after etching with a low etching rate contains an RuO_x layer.

Acknowledgements

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