

Dry Etching of Ru Electrodes using O₂/Cl₂ Inductively Coupled Plasmas

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The characteristics of Ru etching using O₂/Cl₂ plasmas were investigated by employing inductively coupled plasma (ICP) etcher. The changes of Ru etch rate, Ru to SiO₂ etch selectivity and Ru electrode etching slope with the gas flow ratio, bias power, total gas flow rate, and source power were scrutinized. A high etching slope (~86°) and a smooth surface after etching was attained using O₂/Cl₂ inductively coupled plasma.

Keywords : Ru, etching, ICP, plasma.

1. Introduction

In recent years, high dielectric materials such as barium strontium titanate (BST) and tantalum pentoxide (Ta₂O₅), need to be used for the fabrication of capacitor structure.^{1),2)}

Although platinum (Pt) has commonly been utilized as an electrode material, Pt has a difficulty in patterning and thus in forming a bottom electrode. Several research groups have reported that obtaining a sufficient etch selectivity of Pt to the mask material is extremely difficult.³⁾⁻⁶⁾

On the other hand, ruthenium (Ru) is expected to be patterned by chemical etching because the volatile etch product can be produced during the etching process.^{7),8)} Previous researchers reported that volatile RuO₄ can be generated from the RuO₂ which is an intermediate phase of the Ru etching reaction.

However, there are not many systematic studies on the basic characteristics of Ru etching. In this study, we report the etching characteristics of Ru using O₂/Cl₂ inductively coupled plasma. We investigate the Ru etch rate, the Ru to SiO₂ mask etch selectivity, and the Ru etching slope with varied process conditions including Cl₂/(O₂+Cl₂) gas flow ratio and bias power. We investigate the Ru surface after etching by employing Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM).

2. Experimental

The sample structure was substrate/ TiN 500 Å/ Ru

4000 Å/ TiN layer 600 Å/ SiO₂ mask 3000 Å. The SiO₂ mask, instead of photoresist mask, was used for patterning Ru, because oxygen gas was the main etchant in our experiments. The SiO₂ mask was patterned by CF₄/N₂/Ar gas. The TiN layer was inserted between Ru and SiO₂ mask layer to prevent the contamination of etching chamber during SiO₂ mask etching due to Ru exposure. The TiN layer was patterned by Ar/Cl₂ gas. Since Ru cannot be etched by halogen gases only due to high boiling point of their etch products, we used O₂ and Cl₂ gases, expecting that the volatile RuO₄ is produced.^{7),8)}

A DPS centura ICP tool commercially available from Applied Materials, Inc. has been used. During etching, the Cl₂/(O₂+Cl₂) gas flow ratio was 0.1-0.3, the source power was 1000-1800 W, the bias power was 100-300 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 scanning electron microscope (SEM) was used to measure the Ru etching slope and the Ru to SiO₂ etch selectivity. Ru surface after etching was analyzed by AES, XPS, and TEM.

3. Results and discussion

In order to investigate the characteristic of Ru etching, we have varied the Cl₂/(O₂+Cl₂) gas flow ratio and bias power. Fig. 1 shows the change of Ru etch rate, Ru to SiO₂ mask etch selectivity and etching slope with varying Cl₂/(O₂+Cl₂) gas flow ratio in the range of 0.1 to 0.3, using O₂/Cl₂ inductively coupled plasma. The source power, bias power, total gas flow rate and pressure are set to 1400

W, 2000 W, 100 sccm and 20 mTorr, respectively. We reveal that the maximum etch rate of about 670 Å/min is attained at the Cl₂/(O₂+Cl₂) gas flow ratio of 0.2. The Ru etching slope increases with increasing Cl₂/(O₂+Cl₂) gas flow ratio.

Fig. 2 shows the change of Ru etch rate, Ru to SiO₂ mask etch selectivity, and etching slope with varying bias power in the range of 150 to 300 W, using O₂/Cl₂ inductively coupled plasma. The source power, total gas flow rate and pressure are set to 1400 W, 100 sccm and 20 mTorr, respectively. The Cl₂/(O₂+Cl₂) gas flow ratio is set to 0.2. Both the Ru etch rate and etching slope increases with increasing bias power. However, the Ru to SiO₂ mask etch selectivity decreases with increasing

bias power due to the significant increase of SiO₂ mask etch rate. We assume that etching of SiO₂ mask with O₂/Cl₂ gas proceeds mostly by ion bombardment, because increasing the bias power helps to increase the ion bombardment energy.

In order to investigate the characteristics of Ru etching with varying the radical density, we varied the total gas flow rate and the source power using O₂/Cl₂ inductively coupled plasma. The pressure, bias power, and Cl₂/(O₂+Cl₂) gas flow ratio are set to 20 mTorr, 200 W, and 0.2, respectively.

Fig. 3 (a) shows that Ru etch rate, Ru to SiO₂ mask etch selectivity, and etching slope increases with increasing total gas flow rate in the range of 100 to 400

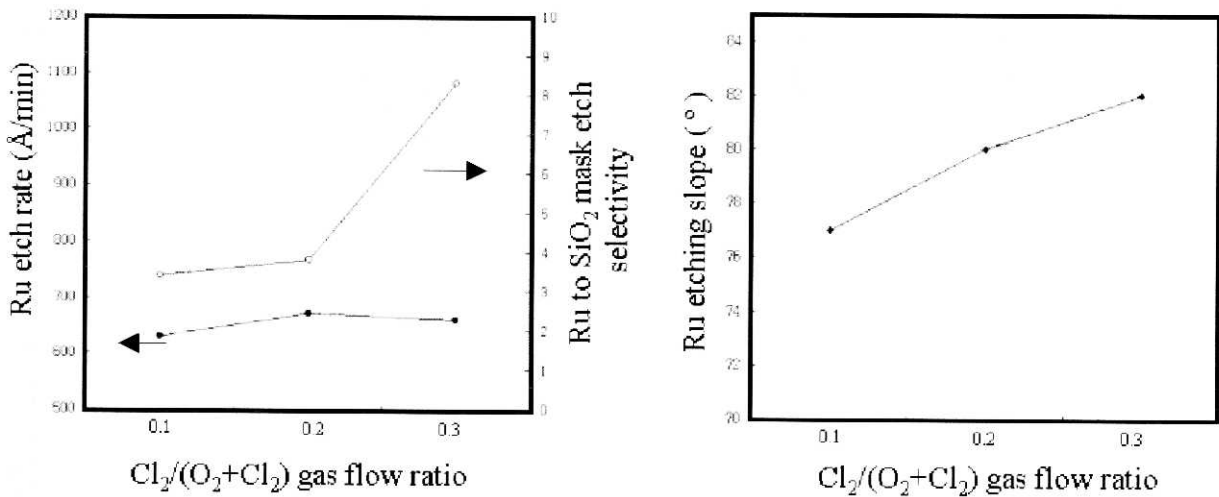


Fig. 1. Variation of Ru etch rate, Ru to SiO₂ mask etch selectivity and etching slope with varying Cl₂/(O₂+Cl₂) gas flow ratio.

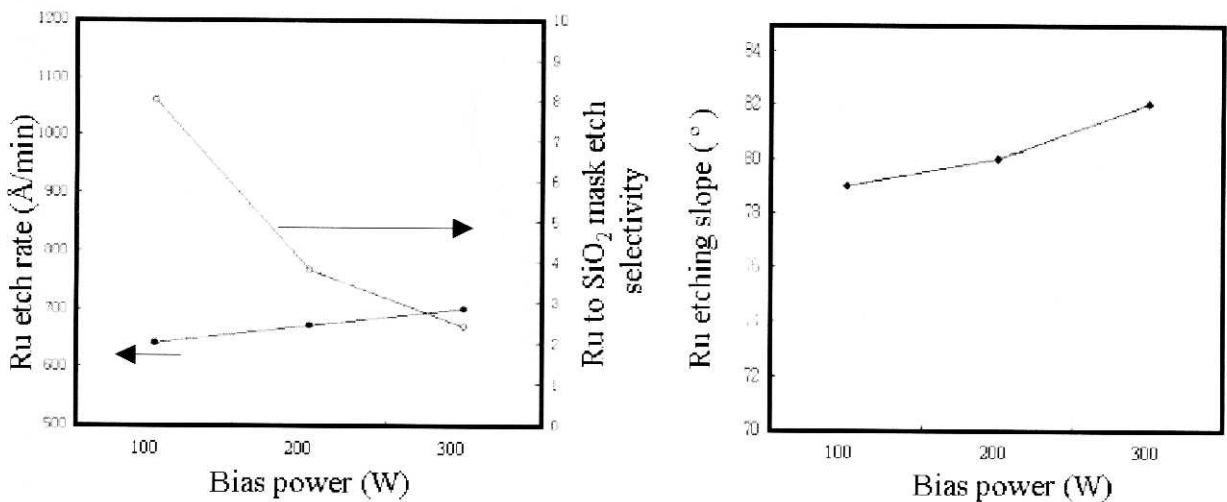


Fig. 2. Variation of Ru etch rate, Ru to SiO₂ mask etch selectivity, and etching slope with varying bias power.

sccm. Fig. 3 (b) shows that Ru etch rate, Ru to SiO₂ mask etch selectivity, and etching slope increases with increasing source power in the range of 1000 to 1800 W. We surmise that the amount of radical flux per unit time may increase and thus the Ru etching reaction may be enhanced with increasing gas flow rates and source power. Accordingly, the radical plays an important role in Ru etching process.

We demonstrate the patterning of Ru electrode with a CD of 0.15 μm using O₂/Cl₂ inductively coupled plasma. Fig. 4 shows that the Ru etching slope at the optimized etching condition is measured to be 86°.

Fig. 5 shows a TEM image of a sample etched using O₂/Cl₂ inductively coupled plasma, revealing that no additional layer is formed on top of the Ru surface. The

distance between 2 adjacent crystalline plane of the material both at position "A" and "B" is identical and measured to be about 2.4 Å, corresponding to the lattice parameter of Ru(100). In order to understand the Ru etching process, we investigated the etched Ru surface using O₂ and O₂/Cl₂ plasma.

We performed an XPS analysis and measured the relative amounts of Ru, O, and Cl elements on the etched Ru surface below the depth of 100 Å. The amount of O and Cl is about 36.8 % and 13.4%, respectively, in case of O₂/Cl₂ plasma (O₂/(O₂+Cl₂)=0.8). The amount of O and Cl is about 55.1 % and 1.9%, respectively, in case of O₂ plasma (O₂/(O₂+Cl₂)=1.0). The relative amount of O element on the Ru surface etched using O₂ plasma is greater than that using O₂/Cl₂ plasma. Also, the relative

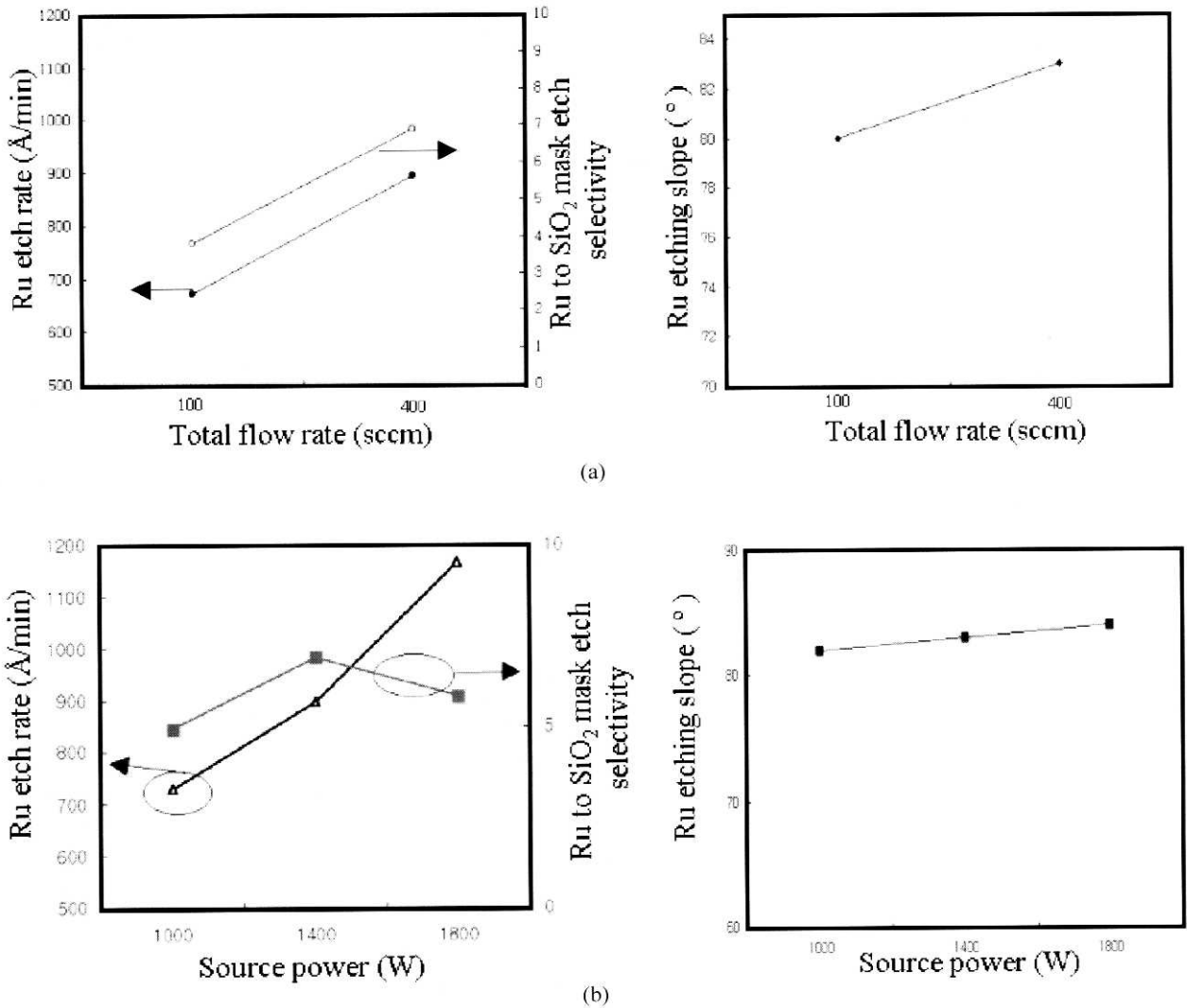


Fig. 3. Variation of Ru etch rate, Ru to SiO₂ mask etch selectivity, and etching slope (a) with varying total gas flow rate in the range of 100 to 400 sccm. (b) with varying source power in the range of 1000 to 1800 W.

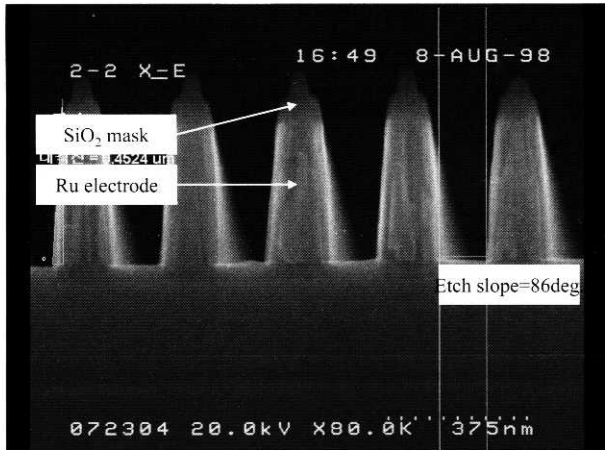
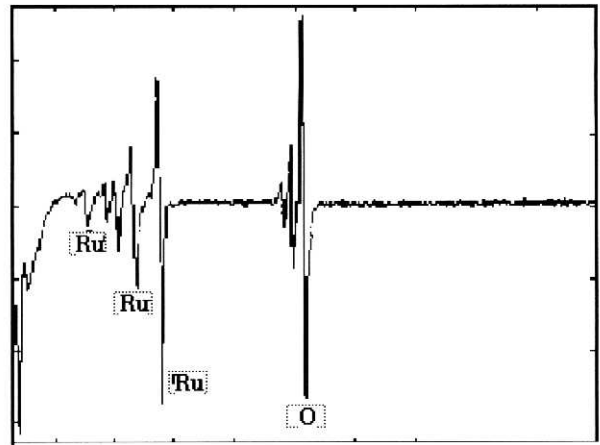


Fig. 4. SEM image of Ru etching profile.



(a)

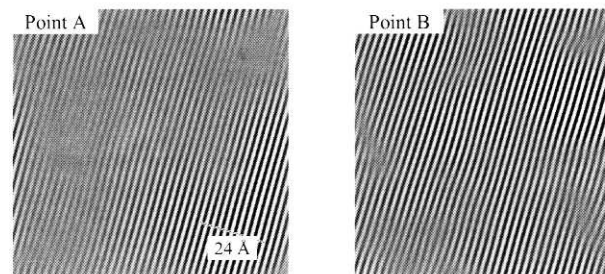
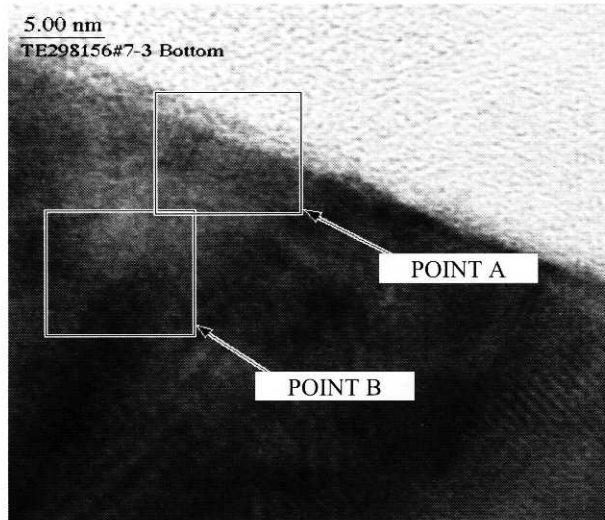
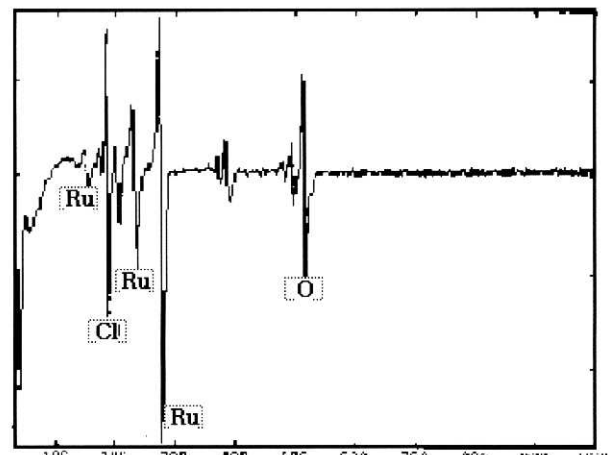


Fig. 5. TEM image of Ru etching profile.

amount of Cl₂ elements on the Ru surface etched using O₂ plasma is smaller than that using O₂/Cl₂ plasma.

Fig. 6 shows the AES spectrum of etched Ru surface. The relative signal of O element compared to Ru element



(b)

Fig. 6. AES spectrum of etched Ru surface (a) using O₂ plasma and (b) using O₂/Cl₂ plasma.

is greater when etched using O₂ plasma than when etched using O₂/Cl₂ plasma. AES spectra agree with an XPS measurement. We surmise that Ru etching proceeds by generation of RuO₂ from Ru, and subsequent generation of volatile RuO₄ from RuO₂. Further study is necessary to reveal the detailed etching mechanism.

4. Conclusions

The characteristics of Ru electrode etching by inductively coupled O₂/Cl₂ discharges is studied. The

variation of Ru etch rate and Ru etching slope by varying process parameters such as $\text{Cl}_2/(\text{O}_2+\text{Cl}_2)$ gas flow ratio, bias power, source power and total gas flow rate have been investigated. A high etching slope of Ru electrode was attained using the ICP plasma. We reveal that the Ru surface after etching using ICP plasma contains no RuO_x layer. The Ru etched surface using O_2 plasma has a greater amount of O element than that using O_2/Cl_2 plasma.

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