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Study of Ru etching using O_2/Cl_2 helicon plasmas

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Abstract

We have investigated the characteristics of ruthenium (Ru) etching using O_2/Cl_2 helicon plasmas, resulting in the high Ru etch profile (> 85°) and the optimal etch rate (> 500 Å min^{-1}). We revealed that the chamber pressure greatly affects the Ru etch rate and Ru to mask etch selectivity. The dependence of Re etch rate on pressure was scrutinized for both patterned and non-patterned wafers. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ru; Etching; Helicon; Pressure

1. Introduction

As dimensions of devices are getting smaller and smaller, high dielectric materials, such as barium strontium titanate (BST), tantallium pentoxide (Ta_2O_5), need to be used for the fabrication of dynamic random access memory (DRAM) capacitors [1–4].

Although platinum (Pt) has been usually 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 [5–7]. On the other hand, ruthenium (Ru) is expected to be patterned by chemical etching because the volatile etch product can be produced [8,9].

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 O_2/Cl_2 helicon plasmas. We investigate the Ru etch rate and the Ru to SiO_2 mask etch selectivity with varied process conditions including pressure, source power, bias power, and $Cl_2/(O_2+Cl_2)$ gas flow ratio. The ion current densities are measured at different pressures and the dependence of Ru etch rate on the ion current density is investigated for patented and blanket wafers. We observe the Ru surface after etching with two different process conditions, one with a fast etch rate and the other with a slow etch rate, in order to study the etching mechanism.

2. Experiments

Schematic diagram of an $m = 0$ helicon plasma reactor used in this study is described in Fig. 1. Helicon wave plasma sources were operated at the excitation frequencies of 13.56 MHz. The diameter of the process chamber covered by 24 cusp magnets along the chamber axis was 350 mm. The helium pressure was 20 Torr and both the inner and the outer currents were 40 A. During etching, the source power was 1000–2000 W, the bias power was 150–250 W, the magnetic field was 100–200 G and the total gas flow rate was set to 300 sccm.

We used the 8-inch wafers, which were either patterned or non-patterned (blanket). The patterned wafers with a critical dimension (CD) of 0.15 nm were used. The sample structure was substrate/TiO_2 600 Å/Ru 4000 Å/SiO_2 mask. The ion current densities of the plasmas were monitored by a Langmuir probe at the position of substrate holder. SiO_2 mask, instead of 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.

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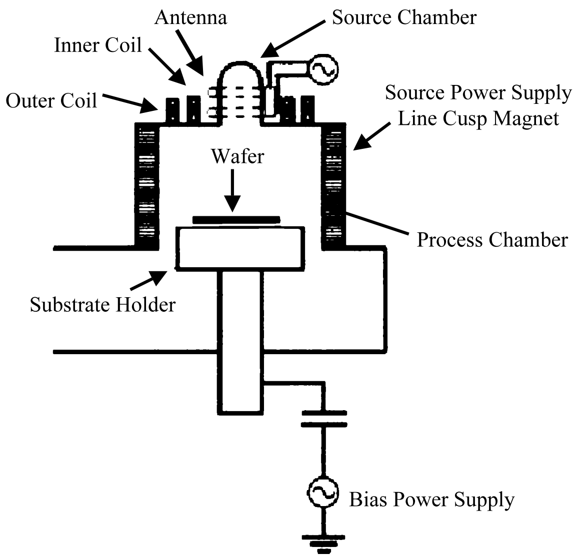

Fig. 1. Schematics diagram of a helicon chamber.

As Ru cannot be etched by halogen gases due to high boiling point of their etch products, we used O_2 gas as a main etchant, expecting that the volatile RuO_4 is produced [8,9]. The Cl_2 gas was added to enhance the etch rate.

A scanning electron microscope (SEM) was used to evaluate the etched Ru electrode and measure the Ru to SiO_2 etch selectivity. Ru surface after etching was analyzed by Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM).

3. Results and discussions

We investigated the change of Re etch rates with varied $Cl_2/(O_2+Cl_2)$ gas flow ratio. Fig. 2 shows that the Ru etch rate is about 100, 400, 560, and 50 Å min^{-1}, respectively, when the $Cl_2/(O_2+Cl_2)$ gas flow ratio is 0, 6.7, 20, and 100%. The maximum etch rate is attained at 20% of $Cl_2/(O_2+Cl_2)$ gas flow ratio.

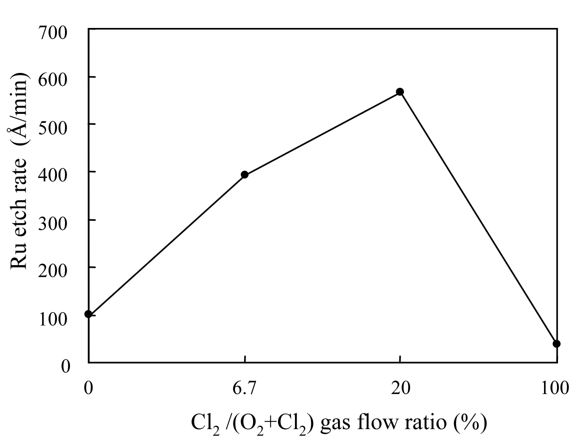

Fig. 2. Ru etch rates as a function of $Cl_2/(O_2+Cl_2)$ gas flow ratio.

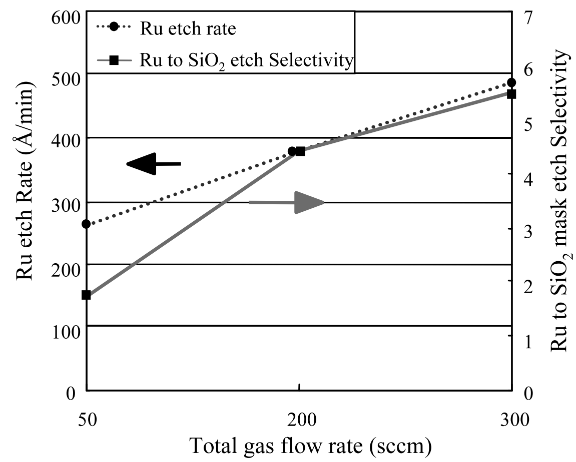

Fig. 3. Ru etch rates and Ru to SiO_2 mask etch selectivities as a function of total gas flow rate.

Fig. 3 shows the etching characteristics depending on the total flow rate, revealing that increasing the total flow rate enhances the Ru etch rate and the Ru to SiO_2 mask etch selectivity. The amount of the etching species, mostly radicals, is supposed to increase with increasing total gas flow rate and thus the Ru etch rate increases with increasing the radical density. By increasing the source power and bias power, the etch rate was enhanced (not shown here). However, the Ru etch rate does not increase with the increase of bias power beyond 250 W. Since the bias power is proportional to the intensity of ion bombardment, the optimal ion bombardment is needed for efficient Ru etching. The effect of Ar addition to O_2/Cl_2 system is not significant and addition of 60 sccm of Ar to the etching gas system reduce the etch rate to 90% of the original value.

Based on the above result, we optimized the standard etching condition, with the 20% of $Cl_2/(O_2+Cl_2)$ gas flow ratio, 300 sccm of total gas flow rate, 2000 W of source power, and 250 W of bias power. We investigated the effect of chamber pressure on the Ru etch rate and the Ru to SiO_2 mask etch selectivity at the optimized condition. As shown in Fig. 4, the Ru etch rate and Ru to SiO_2 mask etch selectivity increase with increasing pressure.

Fig. 5 shows the SEM image of the Ru etching profiles, revealing that the pressure affects both the etch slope and the etch selectivity. At the pressure of 10 and 30 mTorr, the Ru etch slope is about 45 and 85°, respectively. At the pressure of 10 and 30 mTorr, the Ru to SiO_2 mask etch selectivity is about 1 and 5.5, respectively. We obtain the higher etch slope and smooth surface due to the higher Ru etch rate and Ru to mask etch selectivity at higher-pressure range.

To explore the etching characteristics of Ru etching in connection with chamber pressure, we measured the ion

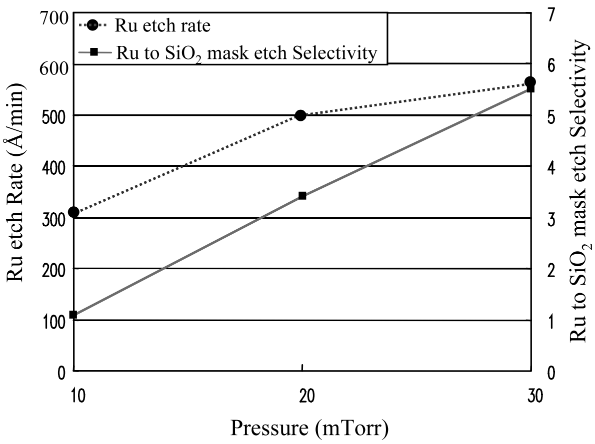

Fig. 4. Ru etch rates and Ru to SiO_2 mask etch selectivities as a function of pressure.

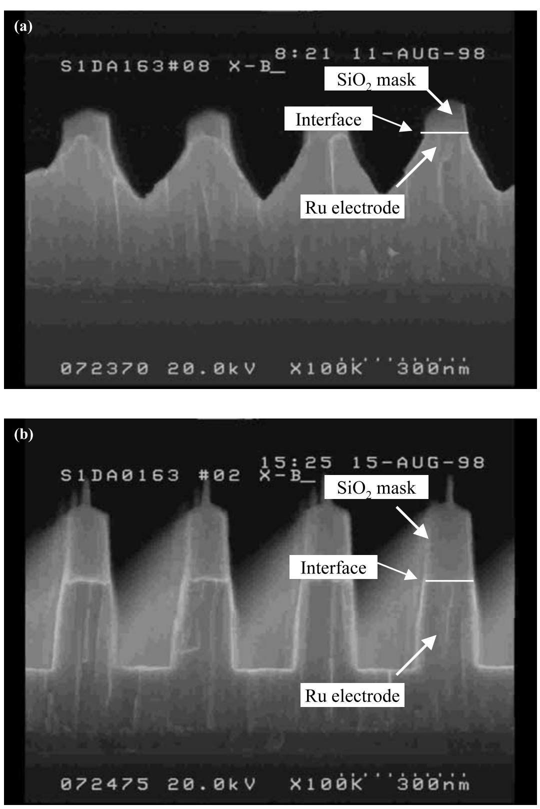

Fig. 5. Ru etching profile at (a) 10 and (b) 30 mTorr. The etching condition with the 20% of $Cl_2/(O_2+Cl_2)$ gas flow ratio, 300 sccm of total gas flow rate, 2000 W of source power, and 250 W of bias power, is applied.

current densities with varied pressure at different source powers. The ion current density was measured by putting the probe near the electrostatic chuck system. Fig. 6 indicates that the ion current density increases with decreasing chamber pressure irrelevant to source power.

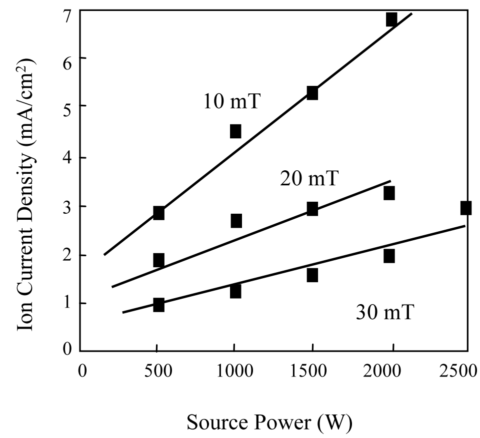

Fig. 6. Ion current densities as a function of pressure at various source powers. The etching condition with the 20% of $Cl_2/(O_2+Cl_2)$ gas flow ratio, 300 sccm of total gas flow rate, and 250 W of bias power, is applied.

We investigated the Ru and SiO_2 mask etch rates with varying ion current density for both blanket and patterned wafers. When the pressures are 30 and 10 mTorr, the ion current densities are 2 and 6.5 mA cm^{-2}, respectively. In case of patterned wafers, while the SiO_2 mask etch rate increases with increasing the ion current density, the Ru etch rate decreases with increasing the ion current density (Fig. 7(a)). At low pressure (10 mTorr), the energy can be transferred without collision and more radicals might be dissociated into ions. By physical sputtering, the resputtering of Ru occurs and the elevation of etch rate is limited. At high pressure (30 mTorr), more radicals exist with less dissociation and the greater amount of volatile RuO_4 can be generated, resulting in an enhanced etch rate.

In case of blanket wafers, both the Ru and SiO_2 etch rates increase with increasing the ion current density. Fig. 7(b) shows that the Ru etch rates are about 350 and 200 Å min^{-1}, respectively, at the ion current density of 5–6 and 1 mA cm^{-2}. By comparing Fig. 7(b) with Fig. 7(a), we reveal that the Ru etch rates at 30 mTorr (5–6 mA cm^{-2}) are 500 and 200 Å min^{-1}, respectively, for patterned and blanket wafers. At 10 mTorr (1 mA cm^{-2}), on the other hand, the Ru etch rate of the patterned wafer is similar to that of the blanket wafers. As the SiO_2 etch rate is relatively small compared to the Ru etch rate, we suppose that the SiO_2 mask etching process does not affect the Ru etching process. We surmise that the radicals play a crucial role in Ru etching using O_2/Cl_2 helicon plasmas at a chamber pressure of 30 mTorr. Although the radicals at a pressure of 30 mTorr are relatively abundant in our helicon etching system, it is still not enough to etch all areas of the exposed area in blanket wafers, implying that the source-limited etching occurs. On the other hand, at 10 mTorr, the amount of radicals is very small and moreover the radicals are easily dissociated into

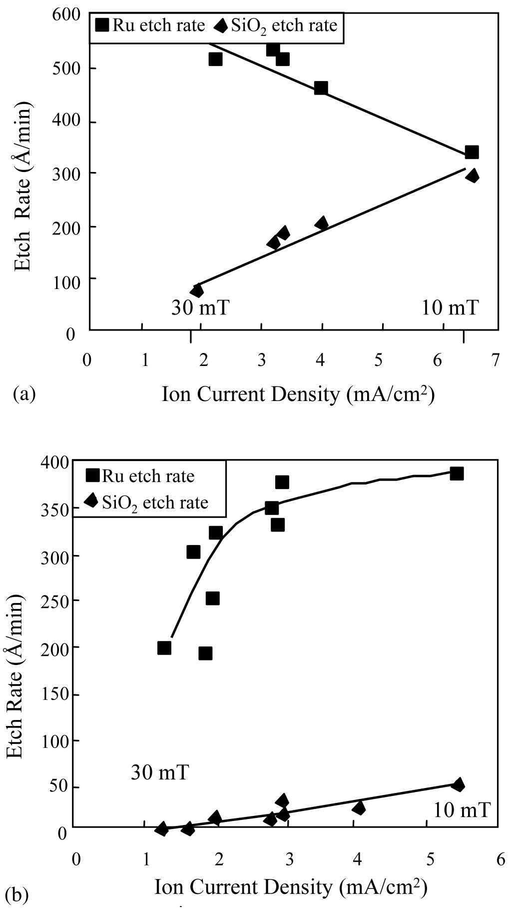

Fig. 7. Ru etch rate as a function of ion current density using (a) patterned wafers and (b) blanket wafers.

Table 1
Post-etch Ru surface analysis with XPS (~ 100 Å)

	Ru (%)	O (%)	Cl (%)
Sample a	54.5	41.1	4.3
Sample b	38.0	60.4	1.6

ions, thus the ions should have played a role and the radicals may not play a crucial role in Ru etching. Therefore, at 10 mTorr of chamber pressure, the amount of radicals does not affect the Ru etching, resulting in the independence of Ru etch rate to etching area.

To systematically investigate the effect of the exposed etching area on the Ru etch rate at 30 mTorr, where Ru etching occurs effectively, we used three different kinds of wafers; (A) Ru blanket wafer (100% exposed) (B) patterned wafer (about 50% exposed) (C) patterned wafer (about 10% exposed). The standard etching process was employed at the pressure of 30 mTorr and the Ru etch rate was (A) 200 (B) 500 (C) 750 Å min^{-1}. The amount of radicals is not sufficient in our helicon etching system, resulting in the shortage of radicals when blank wafers are used. This result agrees with Fig. 7.

To clarify the effect of efficient etching on Ru surface, we used two samples with different etching conditions: (a) when the Ru etch rate is above 500 Å min^{-1}, (b) when the Ru etch rate is below 200 Å min^{-1}. We employed AES and XPS to determine the relative amounts of Cl and O on the Ru surface after the etching processes. AES data shows that the amount of surface oxygen in sample b is greater than that of the surface oxygen in sample a. XPS data reveals that oxygen was detected on the Ru surface below the depth of 15 and 100 Å, respectively, in sample a and sample b. The relative amounts of O and Cl elements on the Ru surface below the depth of 100 Å are shown in Table 1. High resolution TEM reveals that the RuO_2 layer is observed on the Ru surface of sample b (not shown here). On the other hand, no RuO_x is observed on the Ru surface of sample a. We surmise that in the Ru etching, the formation of volatile RuO_4 from RuO_x is a crucial step and if it does not proceed properly, RuO_x layer can be observed. Further systematic studies are needed to understand the detailed mechanism.

4. Conclusion

The Ru electrode with a high etch profile (> 85°) and an optimal etch rate (> 500 Å min^{-1}) has been successfully patterned by O_2/Cl_2 plasmas in a helicon etcher. We have investigated the characteristics of Ru etching by varying the process variables. The pressure greatly affects the Ru etch rate and Ru to mask etch selectivity. The ion current density measurement shows that the plasma at high pressure is composed of a higher concentration of radicals due to the lower degree of ionization of the feed gases. At high pressure, the source-limited etching occurs when the exposed etching area is large. By observing the post-etch Ru surface, we reveal that the diappearance of RuO_x layer is closely related to efficient Ru etching.

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