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Microelectronic Engineering 69 (2003) 89–96
MICROELECTRONIC ENGINEERING
www.elsevier.com/locate/mee

Investigation into patterning of a stack-type Ru electrode capacitor

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Received 26 October 2002; received in revised form 27 February 2003; accepted 7 April 2003

Abstract

We have investigated the characteristics of etching processes involved in the fabrication of the stack-type DRAM capacitor. The 4000-Å high Ru electrode and the SiO_2 hard mask with a critical dimension of 0.15 kHz were employed. The Ru etch rate and the Ru to SiO_2 mask etch selectivity increased by increasing pressure, total gas flow rate, and by addition of Cl_2 gas. We have removed the SiO_2 mask residues using Ar/CHF_3 plasmas, revealing that high RF power helps to remove the residue efficiently.

Keywords: Ru; Etching; SiO_2 mask; Scanning electron microscopy

1. Introduction

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

Capacitors based on dielelectric materials need to employ electrode materials, which should remain stable during the fabrication process. For this reason, noble metals and refractory oxides such as platinum (Pt), ruthenium (Ru), and ruthenium oxide (RuO_2) have been intensively considered. Although Pt has been usually investigated as an electrode material, Pt has an etching problem. Several research groups have reported that obtaining the sufficient etching slope of Pt electrode is very difficult due to the sputtering-nature of the Pt etching process [5–9].

On the other hand, Ru or RuO_2 is expected to be patterned by dry etching because the volatile etch

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0167-9317/03/$ – see front matter
doi:10.1016/S0167-9317(03)00275-2

product can be produced [10–14]. In patterning the Ru electrode, the conventional photoresist mask cannot be used because the O_2-based plasma needs to be used for Ru etching. Even though there are some reports on the basic characteristics of Ru etching [12,13], there is rare report on the fabrication of Ru electrode in real device pattern.

In this work, we report on the Ru etching process related to the fabrication of stack-type Ru electrode. We report the etching characteristics of Ru using O_2/Cl_2 helicon plasmas. We investigate the variation of Ru etch rate and the Ru etching slope with varying process conditions including pressure, total gas flow rate, and $Cl_2/(O_2 + Cl_2)$ gas flow ratio. We also investigate the removal process of the remaining SiO_2 mask after Ru etching, by using wet etching or dry etching technique.

2. Experiments

A storage node pattern with a critical dimension (CD) of 0.15 kHz was used in our experiments. 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 and 250 nm, respectively. The sample structure was Si substrate/SiO_2 layer/TiO 600 Å/Ru 4000 Å/SiO_2 mask 2000 Å. For some device wafers, the TiO_2 layer was removed and the Ru electrode layer was directly deposited on the SiO_2 layer. The SiO_2 mask, instead of photoresist mask, was used for patterning Ru, because oxygen gas was the main etchant in our experiments. In another set of experiments dealing with the removal of SiO_2 mask layer, the gate pattern was used.

An e-MxP + chamber, commercially available from Applied Materials, has been used for SiO_2 mask etching. The SiO_2 mask was patterned by $CHF_3/CF_4/N_2$/Ar gas with an RF power of 1100 W and a magnetic field of 30 gauss. The relatively high RF power was employed to obtain the vertical profile of the SiO_2 mask and the high gas flow ratio of CHF_3/CF_4 is employed in order to minimize the bowing and undercut of patterned SiO_2 mask.

Schematic diagram of a helicon plasma reactor used for Ru electrode etching is shown in our previous work [13]. During etching, the source power was set to 2000 W, the bias power was set to 200 W, the pressure ranged from 10 to 30 mTorr and the total gas flow rate ranged from 50 to 300 sccm. The cathode temperature was set to 45 °C and the helium pressure for cathode cooling was set to 15 Torr.

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 [11,12]. The Cl_2 gas was added to enhance the etch rate.

A scanning electron microscope (SEM) was used to observe the top and vertical view of the Ru electrode pattern after etching process. In order to prepare a sample for the vertical SEM observation, a wafer was cut along the short axis of storage node patterns.

3. Results and discussion

3.1. Patterning of Ru electrode layer

To investigate the etching characteristics of Ru electrode using O_2/Cl_2 helicon plasma, $Cl_2/(O_2 + Cl_2)$ gas flow ratio, total gas flow rate, and pressure were varied. Fig. 1a,b shows the change of Ru

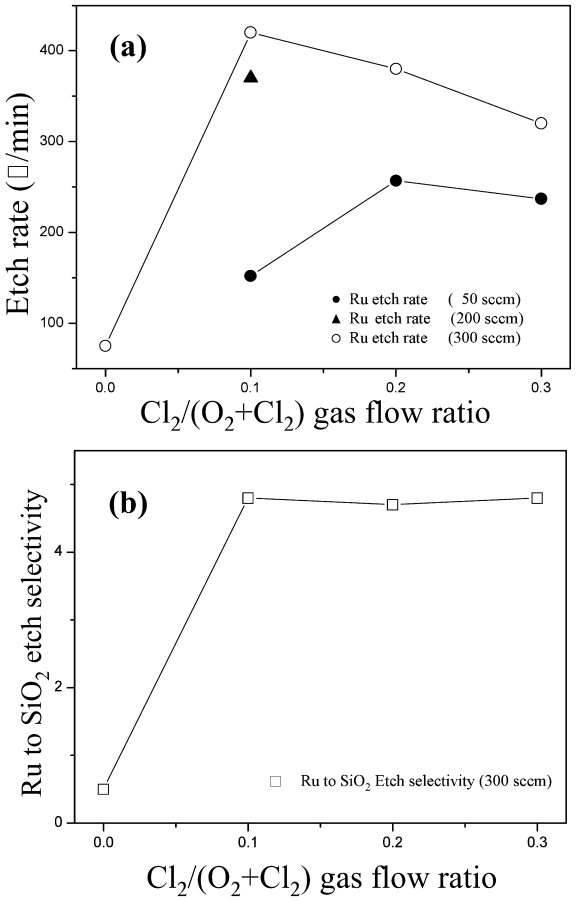

Fig. 1. (a) Change of Ru etch rate by varying $Cl_2/(O_2 + Cl_2)$ gas flow ratio, Pressure ranges from 50 to 300 sccm. (b) Change of Ru to SiO_2 etch selectivity by varying $Cl_2/(O_2 + Cl_2)$ gas flow ratio at a pressure of 300 sccm.

etch rate and the change of Ru to SiO_2 etch selectivity, respectively, by varying $Cl_2/(O_2 + Cl_2)$ gas flow ratio in the range of 0.1 to 0.3, revealing that the Ru etch rate increases from 75 to 420 Å/min by increasing the $Cl_2/(O_2 + Cl_2)$ gas flow ratio from 0 to 0.1 when etched with a total gas flow rate of 300 sccm. Etching with O_2 plasma results in the Ru to SiO_2 etch selectivity of about 0.5 and etching with Cl_2/O_2 plasma results in the Ru to SiO_2 etch selectivity of more than 4, when etched with a total gas flow rate of 300 sccm. Since the Ru etch rate significantly increases by adding Cl_2 gas, we surmise that Cl_2 plays a catalytic role in generating the volatile RuO_2 during the etching process. When etched with a total gas flow rate of 50 sccm, the optimal $Cl_2/(O_2 + Cl_2)$ gas flow ratio increases compared to when etched at 300 sccm.

Fig. 1a also reveals that the Ru etch rate increases by increasing the total gas flow rate ranging from 50 to 300 sccm. When etched with a $Cl_2/(O_2 + Cl_2)$ gas flow ratio of 0.1, the Ru etch rates are 152, 370, and 420 Å/min, respectively, at the pressure of 50, 200, and 300 mTorr. Our experiments reveals that the Ru etch rate and Ru etching slope increase by increasing total gas flow rate [13]. We surmise that the amount of radical flux per unit time may increase and thus the Ru etching reaction may be enhanced with increasing the total gas flow rate.

In order investigate the role of Ar in Ru etching, we have added Ar gas to O_2/Cl_2 plasma. We have added 0, 5, and 10 sccm of Ar gas for comparison study, with the total gas flow rate of 50 sccm. In order to exclude the effect of O_2 or Cl_2, the $Cl_2/(O_2 + Cl_2)$ gas flow ratio is fixed to 0.2 in this experiment. Fig. 2 shows that when $Ar/(O_2 + Cl_2 + Ar)$ gas flow ratios are 0, 0.1, and 0.2, respectively, Ru etch rates are 280, 312, and 337 Å/min. We reveal that the Ru etch rate slightly increases by increasing the $Ar/(O_2 + Cl_2 + Ar)$ gas flow ratio.

In order to investigate the effect of pressure, we have performed the Ru electrode etching at pressures ranging from 10 to 30 mTorr. The total gas flow rate, the $Cl_2/(Cl_2 + O_2)$ gas flow rate, and bias power are set to 300 sccm, 0.2, and 250 W, respectively. Ru etch rates are 300, 500, and 560 Å/min Ru to SiO_2 etch selectivities are 1.1, 3.4, and 5.5 at a pressure of 10, 20, and 30 mTorr, respectively. Ru etching sidewall slopes are 45°, 78°, and 87°, respectively, at a pressure of 10, 20, and 30 mTorr.

Fig. 3 shows SEM images of Ru etching profile at a pressure of (a) 20 mTorr and (b) 30 mTorr. Samples are processed with 20% of an overetch after end point detection (EPD). It is noteworthy that the post-etch Ru surface etched at 20 mTorr is relatively rough compared to the surface etched at 30 mTorr. Furthermore, the amount of remaining SiO_2 mask after the etching process is smaller in case of 20 mTorr. We suppose that the Ru etching using SiO_2 mask at a pressure of 30 mTorr is more efficient than that at 20 mTorr from the above result. Further systematic studies are necessary to reveal the detailed effect of pressure on Ru etching process.

3.2. Removal of mask layer

When the etching process has a high etch selectivity of Ru to SiO_2, SiO_2 mask residues are remaining on top of the Ru electrode as shown in Fig. 3b, even after completing the etching process. We have applied the wet etching technique using a mixture of deionized water and hydrofluoric acid (HF). The process is effective in removing the SiO_2 mask residues but the surface of the Ru electrode

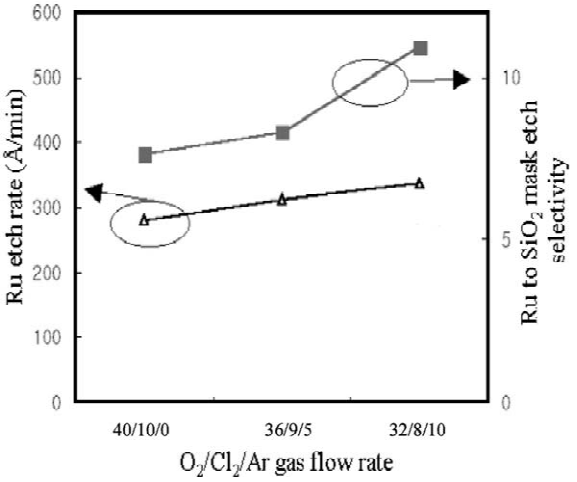

Fig. 2. Change of Ru etch rate, Ru to SiO_2 etch selectivity depending on the $O_2/Cl_2/Ar$ gas flow ratio.

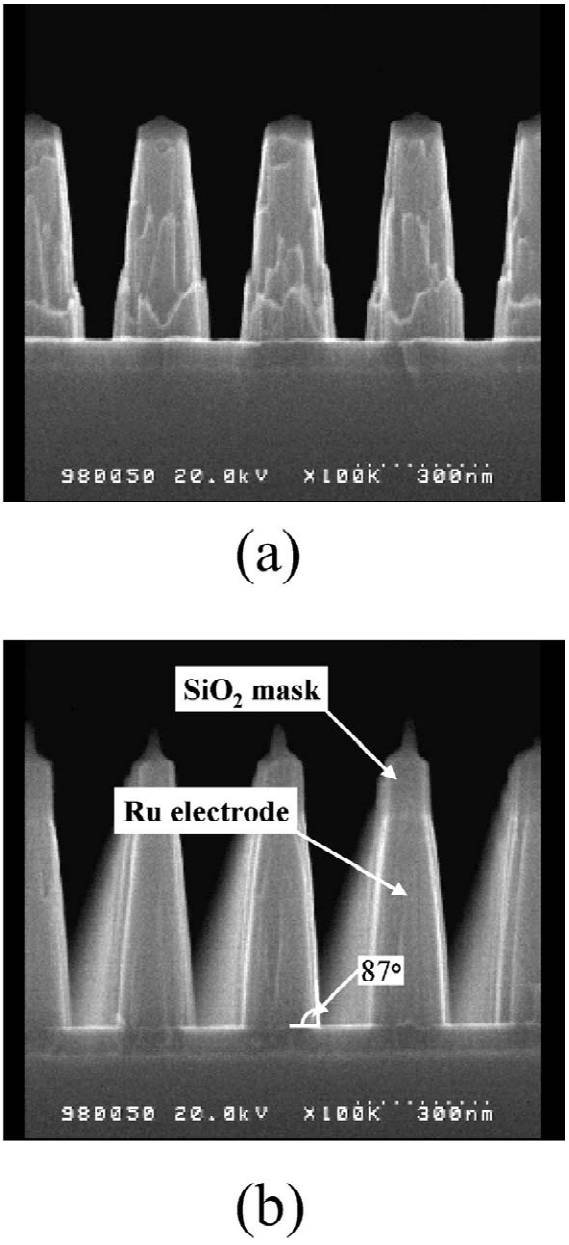

Fig. 3. SEM images of Ru etching profile etched at (a) 20 mTorr and (b) 30 mTorr.

becomes very rough due to the reaction of HF with the Ru atoms. Fig. 4 shows the SEM images of Ru etching profile with the bottom layer of TiO_2. When the bottom layer is SiO_2, the SiO_2 layer is attacked by the HF aqueous solution and the storage node is collapsed (not shown here).

Accordingly, we have performed an experiment to remove the SiO_2 mask residue by plasma etching using Ar/CHF_3 system. We have used a gate electrode pattern in which Ru was partially

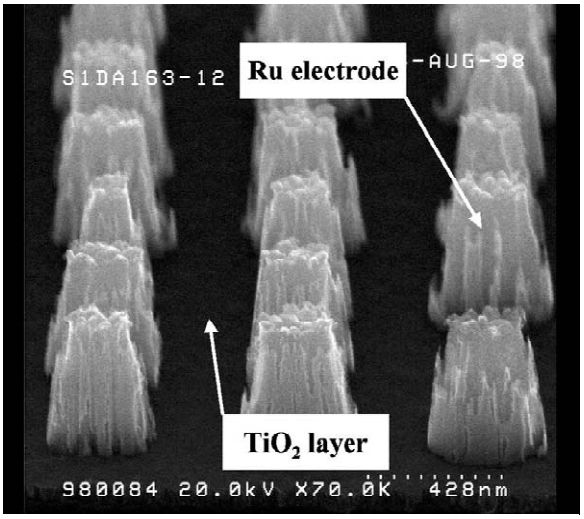

Fig. 4. SEM images of Ru etching profile with the bottom layer of TiO_2.

etched. As shown in Fig. 5a, the mask residues of the irregular shapes are remained even by 100% overetch. We surmise that the mask SiO_2 layer reacts with the Ru surface by the supplied thermal energy during etching process and thus the adhesive RuO_x-type compounds are generated between the mask SiO_2 and Ru surface.

We have performed an experiment to remove the SiO_2 mask residue by elevating the RF power from 250 to 600 W. By applying the high-RF power etching process, the SiO_2 mask sidewall residues on top of Ru electrode are removed completely without the excessive etching. Fig. 5b,c shows the top view and the cross-sectional view of the Ru etching profile with the SiO_2 mask removed by high power etching process. However, it is notable that the Ru etching slope is lowered during the mask removal etching, probably resulting from the resputtering of Ru atoms.

When we use the SiO_2 as a bottom layer instead of TiO_2 layer, considerable amount of the bottom layer is eroded during the mask removal process even by applying the dry-etching method. To overcome this problem, we investigated replacement of the SiO_2 mask layer with the SiON layer. In this case, we performed the Ru electrode etching using the SiON mask and then removing the remaining SiON mask by the optimal etching process which has a sufficient SiON to SiO_2 etch selectivity. Subsequently, we remove the remained mask residue by wet etching method using the phosphoric acid which is expected to have a sufficient SiON to SiO_2 etch selectivity.

4. Conclusion

We have investigated the characteristics of etching processes involved in the fabrication of DRAM capacitors using a stack-type Ru electrode. The variation of Ru etch rate and Ru etching slope by varying process parameters using O_2/Cl_2 helicon plasmas, such as $Cl_2/(O_2 + Cl_2)$ gas flow ratio, total flow rate, and pressure has been investigated. Ru etch rate and Ru to SiO_2 mask etch selectivity increase by increasing the total gas flow rate, and addition of Cl_2 gas, implying the importance of

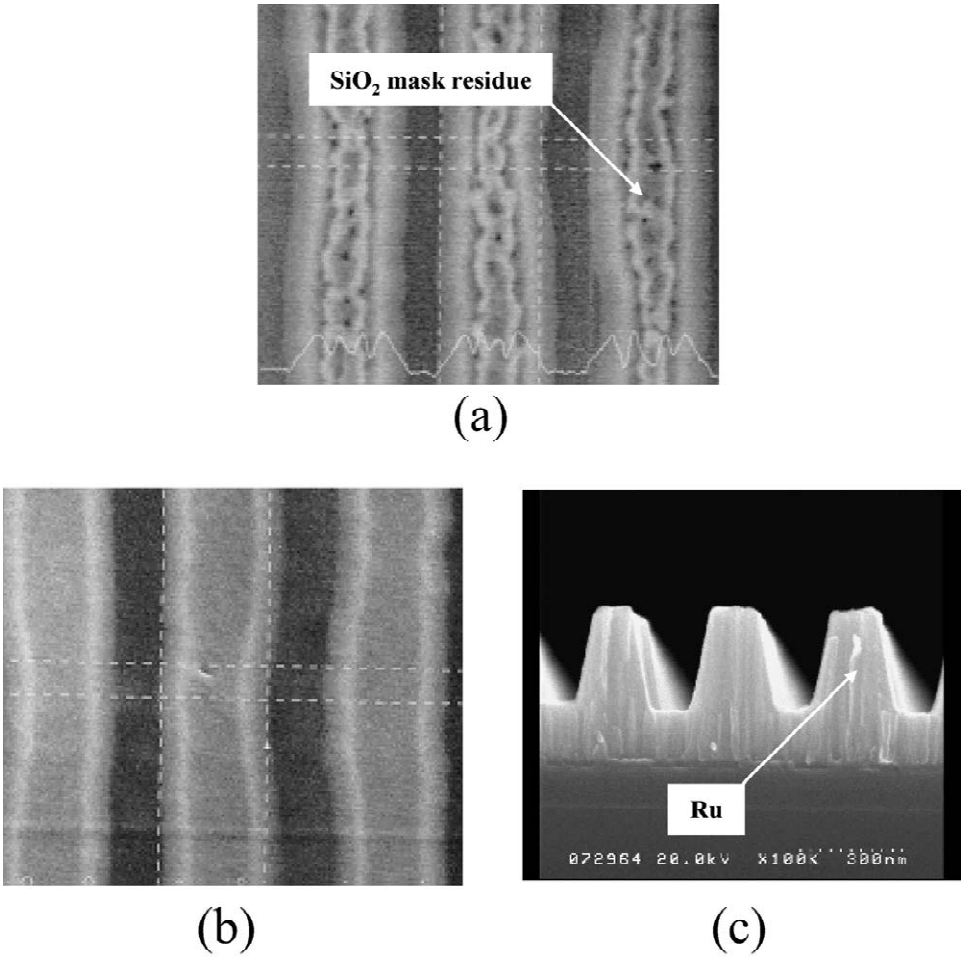

Fig. 5. SEM images of Ru gate patterns showing the removal of SiO_2 mask. (a) Top view of the patterns etched with a low (250 W) RF power. (b) Top view of the patterns etched with a high (600 W) RF power. (c) Cross-sectional view of the patterns etched with a high (600 W) RF power.

chemical reaction for the efficient Ru etching. It is noteworthy that Ru to SiO_2 etch selectivity and thus Ru etching sidewall slope increase by increasing the pressure. In order to remove the SiO_2 mask residues after the Ru etching, we apply both wet etching and dry etching techniques. In the dry etching technique using Ar/CHF_3 plasmas, we reveal that high RF power helps to remove the SiO_2 mask residues efficiently.

Acknowledgements

The authors gratefully acknowledge financial support of present work by Semiconductor Research & Development Center of Samsung electronics Co. We especially thank to Dr. Moon Yong Lee and

Dr. Joo Tae Moon for their advice. Also this work was supported by INHA UNIVERSITY Research Grant through the Special Research Program in 2003.

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