

Submicron SrTiO₃ Patterning by Reactive Ion Etching with Cl₂ and SF₆

Hidemitsu Aoki, Toshiki Hashimoto, Eiji Ikawa, Takamaro Kikkawa,
Shintaro Yamamichi*, Toshiyuki Sakuma* and Yoichi Miyasaka*

Microelectronics Research Labs, NEC Corp.
1129, Shimokuzawa, Sagamihara, Kanagawa 229, Japan

*Fundamental Research Labs, NEC Corp.
1-4-1 Miyazaki, Kawasaki, Kanagawa 213, Japan

A high dielectric constant (ϵ_r) material which allows great charge density in a storage capacitor is needed for next generation 256M- and 1G DRAMs. Thin strontium titanate (SrTiO₃) films have features of high ϵ_r , and chemical and structural stability. Since submicron SrTiO₃ patterning is necessary for realizing future planar DRAM structures, etching reaction for SrTiO₃ film is investigated. It was found that the SrTiO₃ film could be chemically etched by Cl₂ and SF₆ mixture gas, and 0.6 μ m SrTiO₃ patterns were etched by Cl₂ with 10%-SF₆ gases. In addition side wall deposition layer was removed by rinsing with CH₃COOH, HNO₃ and HF mixture.

1. Introduction

As dynamic random access memory (DRAM) cells are scaled down, an advanced storage capacitor fabrication process is required to provide sufficiently large capacitance in a limited area. In order to achieve adequate charge storage within acceptable cell size, silicon oxide/nitride capacitors in conventional DRAMs have to be fabricated by complex processes such as trench or stacked capacitors. High dielectric constant (ϵ_r) material which allows great charge density in a storage capacitor is needed for next generation 256M- and 1G DRAMs. In recent years, several kinds of high ϵ_r materials have been reported. Ferroelectric materials such as lead zirconate titanate and PbTiO₃ have been investigated for nonvolatile memories¹⁻³. Reactive ion etching for PbLaZrTiO₃ at high temperature has also been reported⁴. For DRAM applications, the memory behavior by polarization reversal is not necessarily required, but only the material with high ϵ_r is required for greater charge storage density⁵. Thin strontium titanate (SrTiO₃) films have features of high ϵ_r , and chemical and structural stability^{6,7}. Future planar DRAM structures can be realized by using SrTiO₃ film⁸. Therefore, submicron SrTiO₃ patterning is necessary for suppression parasitic capacitor. However, few dry etching

processes for SrTiO₃ have been reported yet.

In this paper, we investigated reactive ion etching for sub-micron SrTiO₃. Electron Cyclotron Resonance (ECR) plasma was selected for anisotropic etching, because high density plasma under low-pressure could be achieved. Halogen gases were used for forming volatile products.

2. Experimental

The SrTiO₃ thin films were deposited using ion beam sputtering onto thermally oxidized Si substrates. The substrates temperature was maintained at 450°C during SrTiO₃ deposition. Ion beam voltage and ion beam current were 1000V and 40mA, respectively. The deposition rate was 55nm/hour. In this experiment, 0.2 μ m thick-SrTiO₃ films were used in order to study the etching reaction for the SrTiO₃ films. Using ECR etcher, microwave power and gas pressure were held constant at 300W and 1mTorr, respectively. Both RF power for substrate bias and substrate temperature were controlled from 100W to 200W and from -50°C to +40°C, respectively. Multi-layer resist masks, which were composed of photo-resist (thickness: 0.5 μ m)/ spin on glass (0.16 μ m)/ organic-resist (1.2 μ m) were used. Influence of Cl₂ and SF₆ gases on the SrTiO₃ etching were investigated by optical emission spectroscopy.

3. Results and Discussion

Figure 1 shows the dependence of SrTiO₃ film etching rates on RF power with respect to Cl₂ gas and Ar gas. The SrTiO₃ film etching rates by Cl₂ gas is three times greater than that by Ar gas at 150W RF power. The etching by Cl₂ gas should be explained both due physical etching and by chemical etching, because momentum transfer of Cl⁺ ion should be nearly equal to that of Ar⁺ ion.

Figure 2 (a) shows the SrTiO₃ film etched only by Cl₂ gas. The residues were observed in the spaces between SrTiO₃ patterns after etching. By adding 5%-SF₆ gas to Cl₂, the residue could not be observed as shown in Fig. 2 (b). Figure 3 shows the dependence of the SrTiO₃ film etching rate on SF₆ gas addition (0%-100%). The film etching rate shows a peak at 10%-SF₆ addition, and at 100%-SF₆ gas, the film etching rate is one third of that using 100%-Cl₂ gas. Since this etching rate nearly equals to the etching rate using Ar gas, physical sputter etching is dominant by SF₆ etching. Figure 4 shows the dependence of normalized optical emission intensities for SrCl, SrF, TiF and TiCl on SF₆ gas addition. The intensities for SrCl and TiCl decrease, and the intensity for TiF increases with increasing SF₆ gas, the optical emission for SrF is not observed. As a result, total spectrum has a peak at about 10%-SF₆ addition as shown in Fig. 4. This result is consistent with the fact that SrTiO₃ etching rate has a peak at 10%-SF₆ addition as shown in Fig. 3. Consequently, the SrTiO₃ could be etched through the formation of reaction products such as SrCl, TiCl and TiF. By forming titanium fluoride, the etching rate could be enhanced and etching residue could be suppressed.

Figure 5 shows the dependence of SrTiO₃ etching rate on substrate temperature for Cl₂ with 10%-SF₆ gases and Ar gas, respectively. The etching rate for SrTiO₃ film by Cl₂ gas increases with increasing substrate temperature. On the other hand, the etching rate for Ar gas is independent of substrate temperature. This result indicates that the SrTiO₃ film is chemically etched by Cl₂ and SF₆ mixture gas. Activation energy calculated from the Arrhenius plot in Fig. 5 is 0.55kcal/mol. This value includes activation energies in several kinds of etching stages, such as adsorption of etchant, etching products formation and desorption of products. The stage which has the smallest activation energy among three determines the activation energy of the etching. This etching reaction would be limited by activation energy of desorption process, because the etching products deposited on resist side-wall during the etching. The side-wall film cannot be removed by O₂ ashing treatment as shown in Fig. 6(a). However, it can be easily removed by using the rinsing

with composition of CH₃COOH : HNO₃ : HF = 40 : 20 : 2 for 5 second as shown in Fig. 6 (b).

4. Conclusions

The etching reaction for SrTiO₃ film was investigated. Submicron patterns could be successfully reactive ion etched by a mixture of Cl₂ and SF₆ gases.

Acknowledgements

The authors would like to thank Drs. Hisatsune Watanabe, Masaki Ogawa, Nobuhiro Endo and Mitsuru Sakamoto for their encouragement and advice. Thanks are also due to Drs. Yoshihiro Hayashi and Kiyoshi Takeuchi and Hirohito Watanabe for valuable discussion and Mr. Shinobu Saito and Hiromu Yamaguchi for their support in sample preparation.

References

- 1) J. F. Scott et al., J. Appl. Phys. 64, 787 (1988).
- 2) D. Bondurant and F. Gnädiger, IEEE Spectrum July, 30 (1989).
- 3) N. Abt et al., Ext. Abs. 23nd SSDM, p.189 (1991)
- 4) M. R. Poor et al., Mat. Res. Soc. Symp. Proc. 200, 211 (1991).
- 5) L. H. Parker and A. F. Tasch: IEEE Circuit Devices 6, 17 (1990).
- 6) T. Sakuma et al., Appl. Phys. Lett. 57 2431 (1990).
- 7) S. Yamamichi et al., Jpn. J. Appl. Phys. 30. 9B. (1991) 2193.
- 8) K. Koyama et al., IEDM Tech. Di., p.823 (1991).

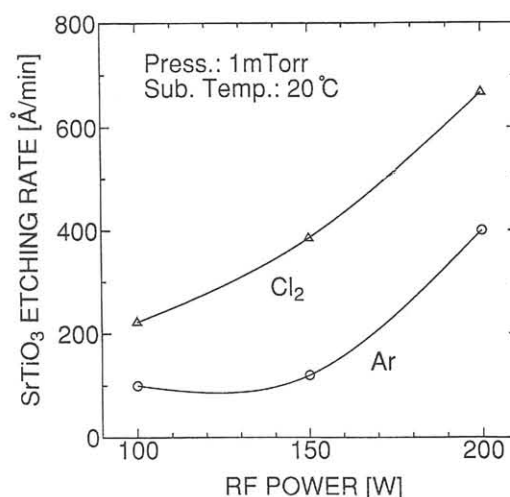


Fig.1 The dependence of SrTiO₃ film etching rates on RF power.

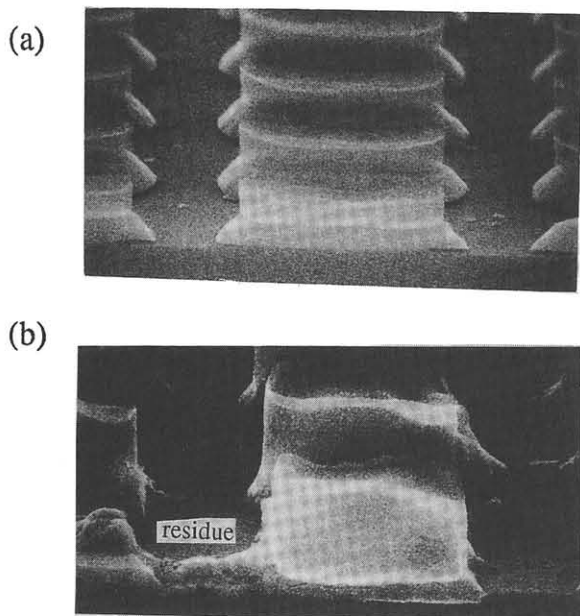


Fig. 2 Cross section SEM micrographs for the SrTiO_3 films etched (a) by only Cl_2 gas (b) by adding 5%- SF_6 to Cl_2 gas.

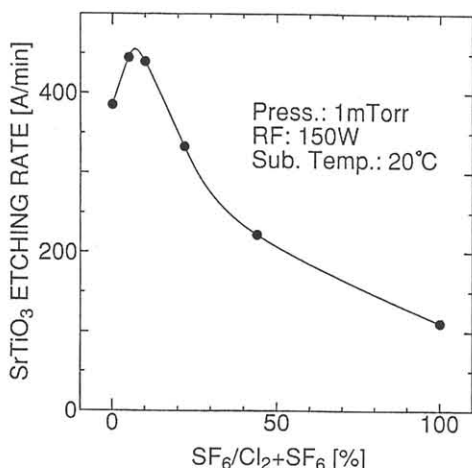


Fig. 3 The dependence of the SrTiO_3 film etching rate on SF_6 gas addition (0%-100%).

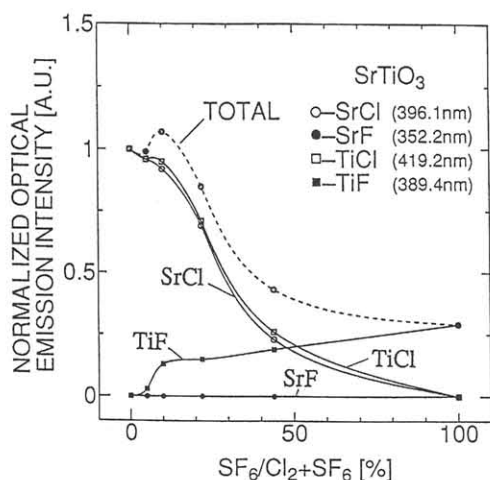


Fig. 4 The dependence of the normalized optical emission intensities for SrCl , SrF , TiF and TiCl on SF_6 gas addition.

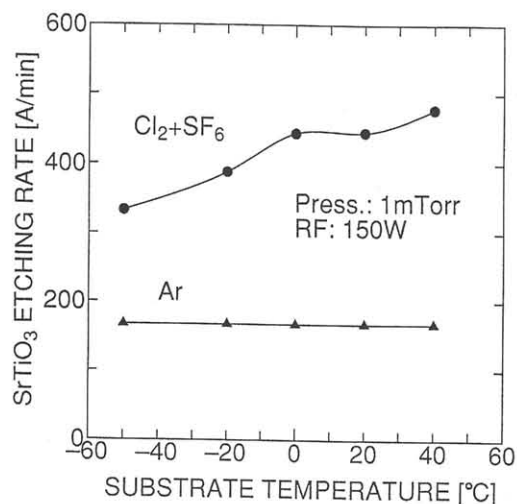
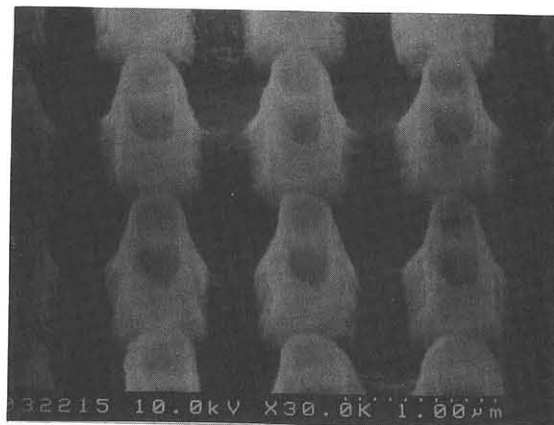


Fig. 5 The dependence of SrTiO_3 etching rate on substrate temperature for Cl_2 gas with 5%- SF_6 gas, and Ar gas.

(a)



(b)

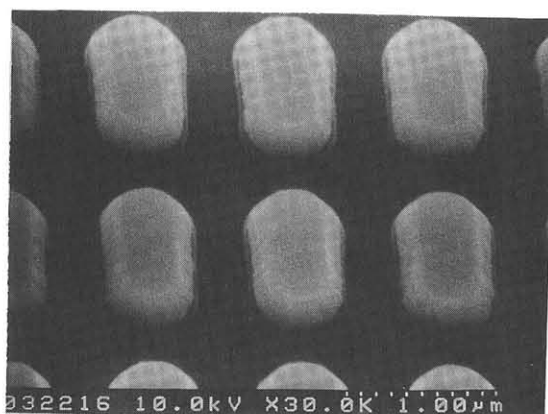


Fig. 6 SEM micrographs of $0.6\mu\text{m}$ SrTiO_3 patterns etched by Cl_2 gas with 10%- SF_6 . (a) after O_2 ashing treatment for 3 minutes. (b) after the rinsing with composition of $\text{CH}_3\text{COOH} : \text{HNO}_3 : \text{HF} = 40 : 20 : 2$ for 5 second and O_2 ashing treatment for 3 minutes.