Submicron SrTiO₃ Patterning by Reactive Ion Etching with Cl₂ and SF₆

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A high dielectric constant (ε₅) 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 ε₅ 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 0.6μm 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 (ε₅) 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 ε₅ material have been reported. Ferroelectric materials such as lead zirconate titanate and PbTiO₃ have been investigated for nonvolatile memories. Reactive ion etching for PbLaZrTiO₅ at high temperature has also been reported. For DRAM applications, the memory behavior by polarization reversal is not necessarily required, but only the material with high ε₅ is required for greater charge storage density. Thin strontium titanate (SrTiO₃) films have features of high ε₅ and chemical and structural stability. Future planar DRAM structures can be realized by using SrTiO₃ film. 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, 0.2μm 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: 0.5μm)/ spin on glass (0.16μm)/ organic-resist (1.2μm) 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 SrTiO$_3$ film etching rates on RF power with respect to Cl$_2$ gas and Ar gas. The SrTiO$_3$ film etching rates by Cl$_2$ gas is three times greater than that by Ar gas at 150W RF power. The etching by Cl$_2$ 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 SrTiO$_3$ film etched only by Cl$_2$ gas. The residues were observed in the spaces between SrTiO$_3$ patterns after etching. By adding 5%-SF$_6$ gas to Cl$_2$, the residue could not be observed as shown in Fig. 2 (b). Figure 3 shows the dependence of the SrTiO$_3$ film etching rate on SF$_6$ gas addition (0%-100%). The film etching rate shows a peak at 10%-SF$_6$ addition, and at 100%-SF$_6$ gas, the film etching rate is one third of that using 100%-Cl$_2$ gas. Since this etching rate nearly equals to the etching rate using Ar gas, physical sputter etching is dominant by SF$_6$ etching. Figure 4 shows the dependence of normalized optical emission intensities for SrCl, SrF, TiF and TiCl on SF$_6$ gas addition. The intensities for SrCl and TiCl decrease, and the intensity for TiF increases with increasing SF$_6$ gas, the optical emission for SrF is not observed. As a result, total spectrum has a peak at about 10%-SF$_6$ addition as shown in Fig. 4. This result is consistent with the fact that SrTiO$_3$ etching rate has a peak at 10%-SF$_6$ addition as shown in Fig. 3. Consequently, the SrTiO$_3$ 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 SrTiO$_3$ etching rate on substrate temperature for Cl$_2$ with 10%-SF$_6$ gases and Ar gas, respectively. The etching rate for SrTiO$_3$ film by Cl$_2$ 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 SrTiO$_3$ film is chemically etched by Cl$_2$ and SF$_6$ mixture gas. Activation energy calculated from the Arrhenius plot of 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 O$_2$ ashing treatment as shown in Fig. 6 (a). However, it can be easily removed by using the rinsing with composition of CH$_3$COOH : HNO$_3$ : F-F = 40 : 20 : 2 for 5 second as shown in Fig. 6 (b).

4. Conclusions

The etching reaction for SrTiO$_3$ film was investigated. Submicron patterns could be successfully reactive ion etched by a mixture of Cl$_2$ and SF$_6$ gases.

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References


Fig.1 The dependence of SrTiO$_3$ 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.

Fig. 6 SEM micrographs of 0.6µm 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 CH$_3$COOH : HNO$_3$ : HF = 40 : 20 : 2 for 5 second and O$_2$ ashing treatment for 3 minutes.