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High Temperature Etching of PZT/Pt/TiN Structure by High Density ECR Plasma

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The submicron patterning technologies for the PZT/Pt/Ti/TiN/Ti structure with a SOG mask was demonstrated using a high density ECR plasma and a high substrate temperature above 300°C. A 30%-Cl_2/Ar gas was used to etch a PZT film. No deposits remained, which resulted in the etched profile more than 80°. The 40%-O_2/Cl_2 gas was used to etch a Pt film. The etching was completely stopped at the Ti layer. The 30 nm thick deposits remained on the side wall. It was removed after dipping in the acid solution. And the etched profile of a Pt film was more than 80°. The Ti/TiN/Ti layer was etched with the pure Cl_2 gas. The CD loss was less than 0.1 μm. The interdiffusion between SOG and PZT was not found by the TEM analysis.

I. Introduction

Significant research and development have recently focused on ferroelectric RAM (FRAM) capable of non-volatile memories[1)-3)]. Thin films of $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) are most notable as FRAM capacitor materials because their remanent polarization (P_r) is large and their coercive field (E_c) is small enough for use as integrated non-volatile memories. Since PZT films are deposited on the bottom electrode in the high temperature oxygen-containing ambient, platinum has been expected for the bottom electrode material[4)5)]. The stacked cell structure, in which a PZT capacitor is made over a pass transistor via a poly-Si contact plug as shown in figure 1, should be introduced to the highly integrated FRAM. However, since a Pt bottom electrode is easily reacted with a poly-Si plug during the PZT processing, a diffusion barrier layer is required between Pt and poly-Si[6)]. Therefore the establishment of patterning technologies for the PZT/Pt/barrier layer structure is indispensable. As far, since PZT and Pt would not easily react with etching gases, the deposits on the side wall of the etching masks cause the severe CD loss. In this report, a high density ECR plasma and a high substrate temperature above 300°C was used in order to accelerate the reaction[7)], which realized the precise patterning of PZT/Pt/Ti/TiN/Ti structure.

II. Experimental Procedure

A high density ECR plasma etching apparatus utilized in this study is shown schemati-

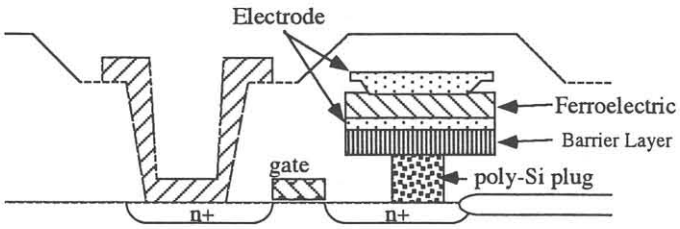


Fig. 1 Stacked Cell Structure of FRAM

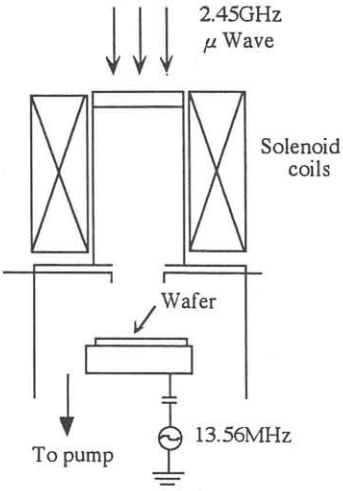


Fig.2 ECR Etching Apparatus

cally in figure 2. The reaction chamber was pumped to a base pressure of below 10^{-6} Torr with a turbomolecular pump, and then Cl_2, Ar, and O_2 gases were introduced by a MFC. The gas pressure during etching varied between 1.4 and 6 mTorr with a throttling valve. The high density plasma established in a ECR chamber was introduced to a reaction chamber. A 13.56 MHz RF power was supplied to a substrate, which was held at a temperature above 300°C during etching.

Figure 3 shows a schematic cross sectional view of the sample. The 1.2 μm thick SOG mask was adopted because a photoresist mask could not be used at a temperature above 300°C. The thickness of PZT, Pt, Ti, TiN, Ti, and NSG film was 250, 100, 20, 200, 20, and 200 nm respectively.

III. Results and Discussions

III-1. PZT Etching

A Cl_2/Ar gas was used to etch a PZT film, because the chlorides of the metal elements contained in a PZT film are expected to evaporate at a high temperature. Figure 4 shows the cross sectional SEM photographs of an etched profile of PZT film masked with a 2.6 μm wide square SOG pattern, of which (a) shows the profile etched with a pure Ar gas while (b) shows the profile etched with a 30%-Cl_2/Ar gas. Etching was carried out with a gas pressure of 1.4 mTorr, microwave power of 1 kW, RF power of 100 W. The deposits made up of Pb, Zr, and Ti remained on the SOG side wall in case of Ar-etching, while no deposits remained in case of Cl_2/Ar-etching. The low gas pressure resulted in the etched profile more than 80° and the CD loss less than 0.1 μm. Figure 5 shows the etch rate against RF power for SOG, PZT and Pt in case of 30%-Cl_2/Ar etching. As RF power decreases, the etch rate decreases monotonically. The selectivity of PZT to SOG and the selectivity of PZT to Pt against RF power was shown in figure 6. As a RF power decreases to 100 W, the selectivity of PZT to SOG increases up to 3.8 while the selectivity of PZT to Pt does not vary notably.

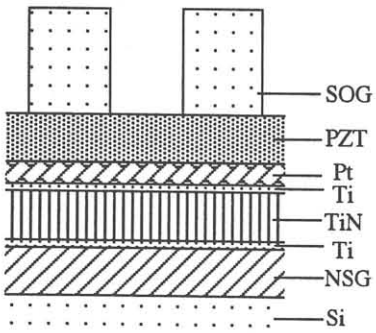
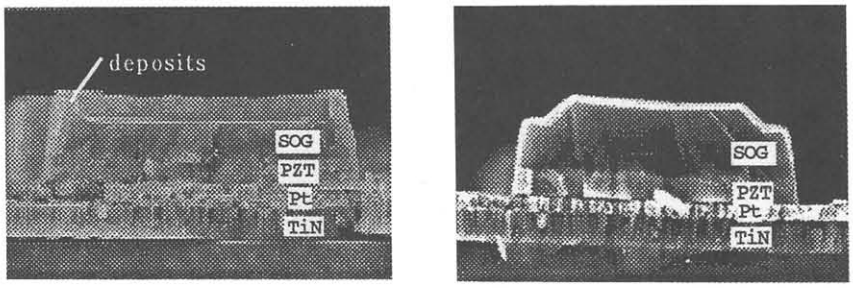


Fig.3 Sample Structure



(a) Ar-Etching (b) Cl_2/Ar-Etching

Fig.4 Etched profile of PZT film

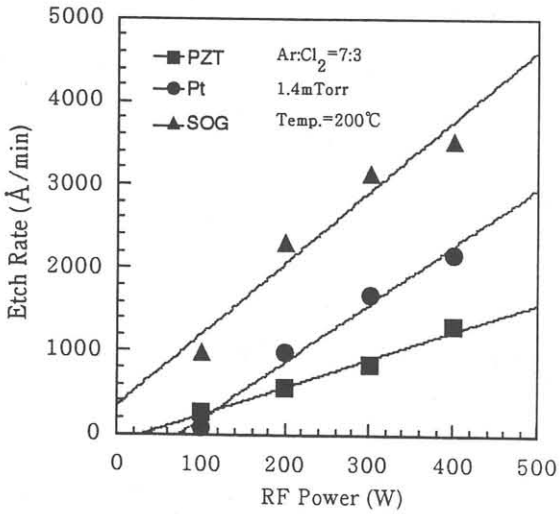


Fig.5 Etch Rate vs RF Power

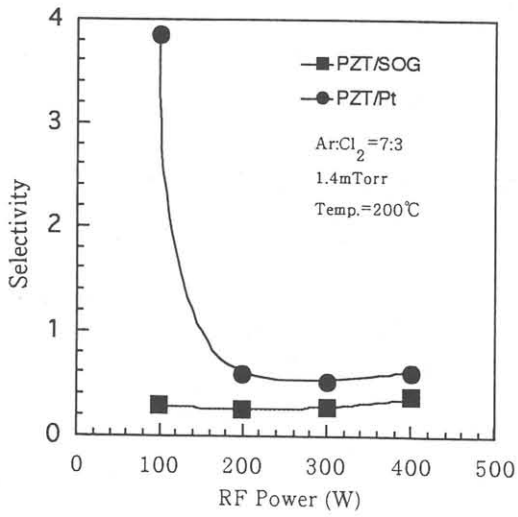
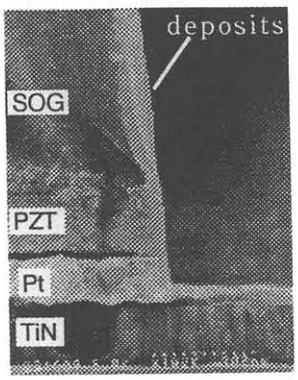
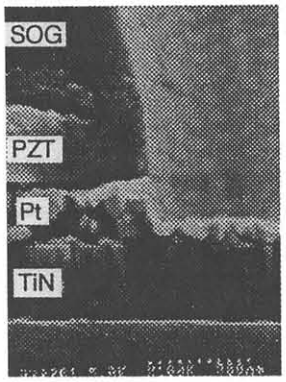


Fig.6 Selectivity vs RF Power



(a)As Etched



(b)After Dipping in the acid solution

Fig.7 Etched Profile of PZT/Pt film

III-2. Pt Etching

The 40%-O_2/Cl_2 gas was used to etch a Pt film. Etching was carried out with a gas pressure of 1.4 mTorr, microwave power of 1 kW, RF power of 200 W. The etch rate of Pt was 90 nm/min. and the etching was completely stopped at the Ti layer. Figure 7 (a) shows the cross sectional SEM photograph of an etched profile of PZT/Pt film. The 30 nm thick deposits remained on the side wall. And presumably it consists of $PtCl_xO_y$, which is well known to be soluble in the acid solution[8]. Figure 7 (b) shows the photograph of the profile after dipping in the acid solution. It reveals that no deposits remained on the side wall and that the etched profile of a Pt film was more than 80°.

III-3. PZT/Pt/Ti/TiN/Ti Structure Etching

Figure 8 shows the cross sectional SEM photograph of an etched profile of PZT/Pt/Ti/TiN/Ti film after the SOG mask was removed. The Ti/TiN/Ti layer was etched with the pure Cl_2 gas and the SOG mask was removed with the CF_4 gas. The CD loss was less than 0.1 μm. The interdiffusion between SOG and PZT was not found by the TEM analysis.

IV. Conclusions

The submicron patterning technologies for the PZT/Pt/Ti/TiN/Ti structure with a SOG mask was demonstrated using a high density ECR plasma and a high substrate temperature above 300°C, which resulted in the accelerated reaction and the precise patterning of PZT/Pt/Ti/TiN/Ti structure.

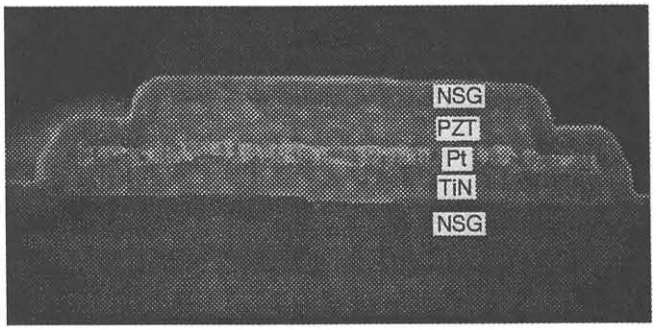


Fig.8 Final Etched Profile of PZT/Pt/Ti/TiN/Ti

V. Acknowledgment

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VI. References

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