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Effect of Ti-Mask Addition and Temperature Elevation on O_2/Cl_2 Plasma Etching of Pt

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We have developed an etching technology for Pt by using a hard mask in a reactive ion etching plasma for future memory applications. We have investigated the effect of insertion of a titanium mask layer between the SiO_2 mask and the Pt layer. Scanning electron microscopy reveals that inserting the Ti layer and increasing the wafer temperature help to elevate the Pt etching slope. A possible mechanism for the improved etching slope is discussed.

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I. INTRODUCTION

In recent years, in addition to the dynamic random access memories (DRAM) which have been developed for volatile memory applications, ferroelectric random access memories (FeRAM) have attracted great attention for non-destructive read-out-type non-volatile memory applications [1–4]. In the application of high dielectric materials, such as $(Ba,Sr)TiO_3$ (BST), for DRAM and ferroelectric materials, such as $Pb(Zr, Ti)O_3$ (PZT) and $SrBi_2Ta_2O_9$ (SBT) thin films, for FRAM, platinum (Pt) is used as a bottom electrode material due to its good oxidation-resistance, high electrical conductivity, and low leakage current [5,6].

Although patterning of PZT or BST has been successfully achieved [7,8], reports on controlled etching of Pt in terms of a sufficiently high etching slope are rare. Since Pt has a low reactivity with the halogen elements and since its etching products havelow vapor pressures, very low etching slopes with sidewall residues have been reported [9]. In such a case, when the space between neighboring capacitors is narrow, the bottom Pt nodes are not separated, resulting in a device malfunction.

In our study, we used O_2/Cl_2 plasmas in a reactive ion etcher for fabricating the Pt bottom electrode with a 0.58-μm critical-dimension pattern. We investigated the effect of Ti mask layer insertion between the Pt and the SiO_2 hard mask and the effect of the wafer surface temperature on the etching slope of the Pt electrode. We observed the Pt electrode by using scanning electron microscopy (SEM) and discuss the possible relationship between the change in the Ti mask layer and the elevation of the Pt etching slope.

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II. EXPERIMENTAL

Figure 1(a) shows the sample structure: substrate/barrier TiN (600 Å)/Pt (2000 Å)/mask Ti (600 Å)/mask SiO_2 (3000 Å). After the oxide mask layer was patterned, the photoresist (PR) was removed. Subsequently, the Ti mask layer, which was located below the oxide mask layer, was patterned with Ar/Cl_2 chemistry by using the SiO_2 mask. Figure 1(b) shows the sample structure before the Pt etching. A reactive ion etcher (RIE) and O_2/Cl_2 gas were used to pattern the Pt, and subsequently, the barrier TiN layer was etched using Ar/Cl_2 gas. The gas flow rates of O_2 and Cl_2 were 40 sccm and 10 sccm, respectively. For comparison, Pt etching was performed with 100 % over-etch after endpoint detection (EPD). During the etching of the barrier TiN, the remaining Ti mask layer on top of the Pt electrode was etched away. Figure 1(c) shows the completed bottom electrode structure before depositing the top electrode layer for DRAM applications.

A heating system with a high-temperature chiller was used for controlling and raising the substrate temperature during etching. A Galden HS 260 solution (boiling point = 270 °C) flowed over the bottom part of the substrate for regulating the temperature. When the chiller temperatures were set to 25 °C and 160 °C, respectively,

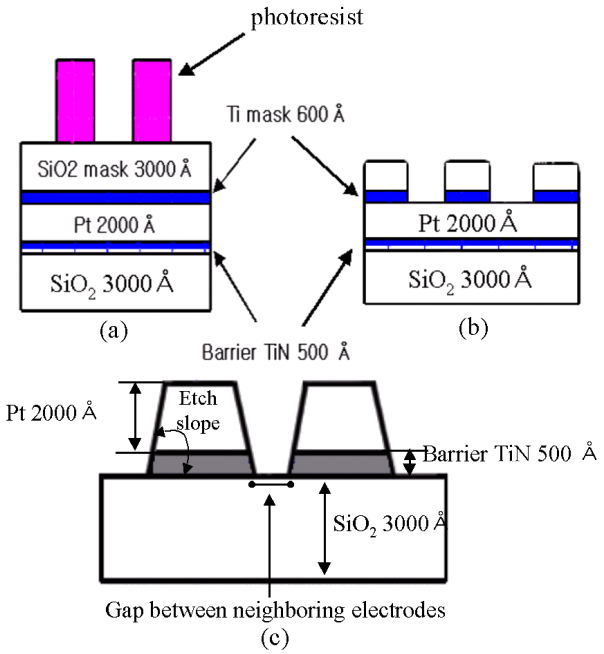

Fig. 1. Sample structure with substrate/TiN (600 Å)/Pt (2000 Å)/Ti(600 Å)/mask SiO_2 (4000 Å) (a) before opening the mask, (b) after opening the SiO_2 and Ti mask, and (c) after Pt etching and subsequent barrier etching.

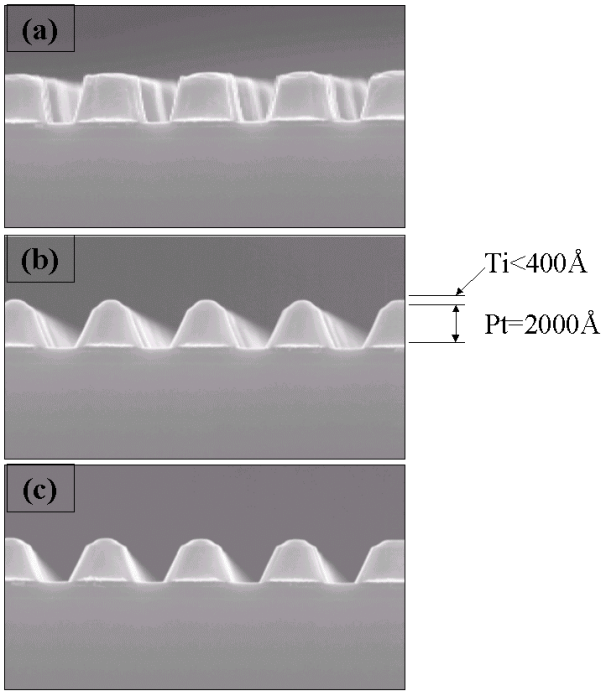

Fig. 2. Cross-sectional SEM images of Pt electrode structures patterned using O_2/Cl_2 plasmas (a) with a TiN mask layer at a substrate temperature of 220 °C, (b) with a TiN mask layer at a substrate temperature of 80 °C, and (c) with a TiOx mask layer at a substrate temperature of 220 °C. All samples were 100 % over-etched after EPD.

and when the plasma was on, the real surface temperatures were measured to be 80 °C and 220 °C. For clarity, the temperature, if not specified, indicates the wafer temperature.

III. RESULTS AND DISCUSSION

In order to investigate the effect of wafer temperature on the Pt etching using O_2/Cl_2 plasma, we performed the patterning experiments at 80 °C and at 220 °C. In the sample structure, the thicknesses of the Ti mask layer and the Pt layer were set to 600 Å and 2000 Å, respectively. Figures 2(a) and 2(b) show the Pt electrode structures patterned at 80 °C and at 220 °C, respectively, with 100 % over-etch after EPD. The Pt etching slope was about 70° at a substrate temperature of 80 °C and about 80° at 220 °C. The thicknesses of the remaining Ti mask layer are $<$ 400 Å and $=$ 600 Å, respectively, at etching temperatures of 80 °C and 220 °C, respectively. Furthermore, the top view of the Pt electrode pattern indicates that the area of the remaining Ti mask layer after Pt etching is larger at the etching temperature of 220 °C than it is at 80 °C. We, thus, surmise that less erosion of the Ti mask layer during etching plays a crucial role in the high Pt etching slope.

In order to investigate the role of the Ti mask layer in increasing the Pt etching slope, we performed Pt etching experiments with titanium nitride (TiN) and titanium oxide (TiOx) hard masks. All samples were 100 % over-etched after EPD with the same O_2 and Cl_2 gas-flow rates. Neither the TiN nor the TiOx mask shows any improvement in the Pt etching slope. Figure 2(c) shows the SEM images of the bottom electrode patterns with a TiOx mask after Pt etching at 220 °C. SEM images indicate that the height of the remaining TiOx mask layer is significantly reduced ($<$ 400 Å) while that of the remaining Ti mask is almost invariant after Pt etching (600 Å).

In order to investigate the effect of gas chemistry on the Pt etching, we varied the $O_2/(O_2+Cl_2)$ gas-flow ratio. SEM image reveals that the Pt etching slope after a 100 % over-etch increases with increasing $O_2/(O_2+Cl_2)$ gas-flow ratio (not shown here). The maximum Pt etching slope was obtained when the $O_2/(O_2+Cl_2)$) gas-flow ratio was unity (*i.e.*, without Cl_2 gas). Since the erosion of the Ti mask layer is minimized and the Pt etching slope is maximized by increasing the $O_2/(O_2+Cl_2)$) gas-flow ratio and the wafer surface temperature and by introducing a pure Ti mask layer, we surmise that an interaction of the Ti layer and the O_2 gas at elevated temperatures contributes to reduced erosion of Ti mask layer.

In order to investigate the changes induced in the Ti layer during the Pt etching process, we employed an O_2/Cl_2 plasma treatment of the Ti surface on the blan-

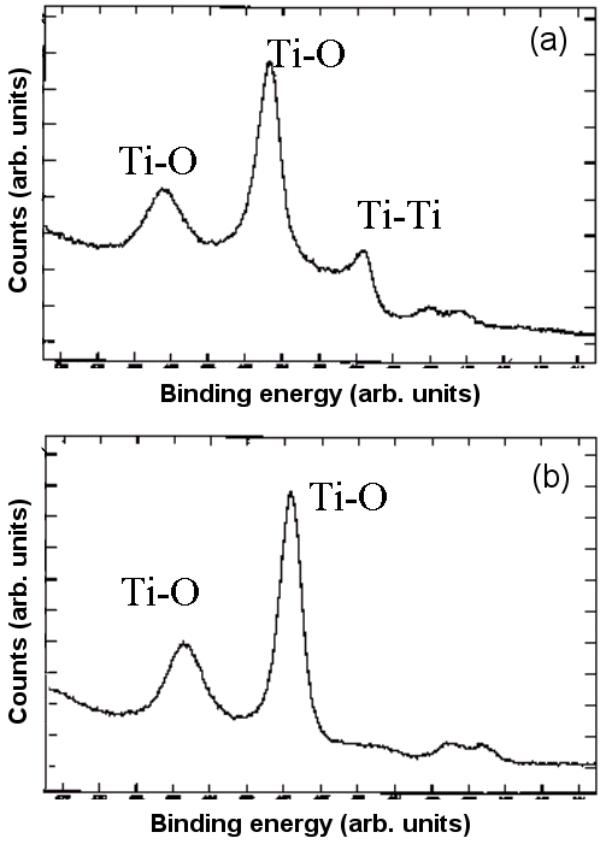

Fig. 3. XPS data for the Ti surface (a) before and (b) after the Pt etching process at 220 °C.

ket wafer at 220 °C. The treatment time and conditions were exactly the same as those for the actual etching process. Figures 3(a) and 3(b) show the X-ray photoelectron spectroscopy (XPS) results for the Ti surface below a depth of about 100 Å, respectively, before and after the Pt etching process at 220 °C. We see that after the Pt etching process, most of Ti-Ti bonding has disappeared and has probably changed to the Ti-O bonding, indicating that the Ti layer has been transformed a TiOx layer down to a depth of 100 Å.

For comparison, we performed the Pt etching treatment on the Ti surface at 80 °C and at 220 °C. Auger electron spectroscopy (AES) was used to plot the relative amounts of Ti and O in the two samples at various depths (not shown here). The boundary layers, where the amounts of Ti and O elements were equal, were situated at depth of 120 Å and 170 Å from the surface, respectively, for the samples etched at 80 °C and at 220 °C. As the depth of the TiOx layer depended on the etching temperature, we surmise that the diffusion of oxygen was enhanced at higher etching temperatures.

It is not clear why oxygen diffusion and the change of the Ti layer to a TiOx layer are related to reduced erosion of Ti mask. Figure 4 showing the Ti mask layer and Pt nodes after etching at 220 °C clearly indicates

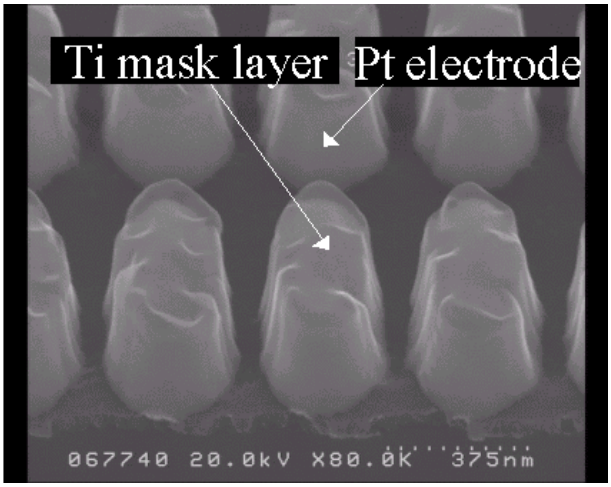

Fig. 4. SEM images showing the bottom electrode patterns after the Pt etching with a Ti mask layer at 220 °C and indicating the severe deformation of Ti mask layer.

severe deformation of the Ti mask layer. It is noteworthy that the improvement in the Pt etching slope and the deformation of the Ti layer occur simultaneously. We estimate that the change of Ti to TiOx during the etching process, with the consumption of oxygen-based etchants, considerably negates the effect of mask erosion. In this case, the Pt etching slope can be increased continuously by sputtering off the Pt atoms with the hard mask remaining. A more systematic study is necessary to reveal the detailed mechanism.

IV. CONCLUSIONS

We have demonstrated that a combination of the Ti mask layer with the oxygen in the plasma at elevated temperatures can contribute to efficient etching of not-etchable materials such as Pt. The Pt etching slope is increased by inserting a Ti mask layer and by elevating the temperature. The Ti mask layer was not eroded after etching, and that was related to the diffusion of oxygen into the Ti layer. The elevation in the Pt etching slope was related to reduced erosion of the Ti mask layer. Not only does this result provide enlightenment for the next generation DRAM and FRAM technonology, but also it is a step in the developing the basic technology for patterning inert materials.

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