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Conformal Platinum Electrodes Prepared by Chemical Vapor Deposition Using a Liquid $MeCpPtMe_3$ Precursor in an Oxidizing Atmosphere

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1. Introduction

Platinum (Pt) exhibits high thermal stability against oxidizing treatment, so it is a promising electrode material for MIM (metal-insulator-metal) capacitors using $(Ba,Sr)TiO_3$ and Ta_2O_5 dielectrics in Gbit-scale DRAMs. Pt thin films have been prepared mainly by reactive sputtering [1]. However, chemical vapor deposition (CVD) producing excellent conformality is required in order to fabricate a three-dimensional capacitor structure [2].

Accordingly, Pt thin films were prepared by CVD using a liquid methylcyclopentadienyl-trimethylplatinum ($MeCpPtMe_3$) precursor [3] in an oxidizing atmosphere. We focused on good conformality of a Pt film with a thickness of less than 30 nm because this film is suitable for the bottom electrodes of a concave capacitor.

2. Experimental

The precursor, $MeCpPtMe_3$, was vaporized at 35°C, at which vapor pressure was about 0.2 Torr. Ar gas was used as a transfer carrier of the precursor, and O_2 gas was mixed with the precursor just before entering the reaction chamber. The O_2/Ar ratio was set at 1/20, 2/1, and 7/1 by changing the flow rates of Ar and O_2 gas. Total pressure was kept at 5 Torr. The substrates were either flat SiO_2(100 nm)/Si or patterned SiO_2/Si with holes of 300-nm diameter and 700-nm depth. The substrate temperature was varied from 200°C to 350°C.

3. Results and Discussion

Figure 1 shows the dependence of film thickness on deposition time. Under the O_2/Ar ratio of 1/20, the film grows proportionally to deposition time but consists of granular grains [Fig. 2(a)], and a large amount of carbon impurities reside in the Pt film [Fig. 3(a)]. This is because the precursor was decomposed thermally and incompletely at low O_2/Ar ratio. On the contrary, under the O_2/Ar ratio of 2/1, the Pt film consists of columnar grains [Fig. 2(b)] with low carbon impurities due to an oxidizing decomposition [Fig. 3(b)]. However, another problem is a long incubation time at the initial growth stage where no films were grown [Fig. 1]. At the highest O_2/Ar ratio of 7/1, Pt film thickness increases linearly, because of the enhanced oxidizing decomposition, so the thickness can be controlled to less than 30 nm. The Pt film grows with a columnar structure and low carbon impurities [Fig. 3(c)] because the precursor was decomposed completely in the highly oxidizing atmosphere.

Very thin Pt films (20-30 nm) were analyzed by a low-angle-incident X-ray method, in which the incident angle was 2° and only the 2θ axis was swept. Figure 4 shows change in the XRD patterns of Pt films grown at the three O_2/Ar ratios, 1/20, 2/1, and 7/1. Diffraction lines from Pt oxide are not observed, and the Pt films are slightly (111)-oriented regardless of the O_2/Ar ratio.

Figure 5 compares cross-sectional SEM images of the Pt films deposited onto concave holes at deposition temperatures between 200°C and 280°C at O_2/Ar ratio of 7/1. The bottom area of the Pt film deposited at 200°C is enlarged in Fig. 6. Conformality is fairly good regardless of deposition temperature. However, the continuous and flat surface changes to discontinuous and granular as deposition temperature increases.

Surface morphology is also affected by film thickness. Figure 7 shows the Pt film morphology deposited at two different thicknesses of 30 and 70 nm and 250°C. The Pt film surface becomes rough and, simultaneously, micro-dendrites grow as the film thickness increases.

Figure 8 summarizes film morphology as functions of film thickness and deposition temperature under the high O_2/Ar ratio of 7/1. Clearly, increasing deposition temperature causes the discontinuous grain growth, and increasing film thickness makes the surface rough and dendritic. It is thus concluded that a Pt film with a smooth surface can be obtained at film thicknesses less than 30 nm and at low deposition temperatures less than 300°C.

4. Conclusion

Conformal CVD-Pt films suitable for MIM capacitor structures were grown under highly oxidizing conditions. A smooth surface was attained at low deposition temperature and when the film thickness is below 30 nm.

References

[1] B.T. Lee et al., IEDM, (1998) p.815.
[2] K. Eguchi et al., SSDM, (1999) p.484.
[3] Z. Xue et al., J. Am. Chem. Soc., 111 (1989) 8779.

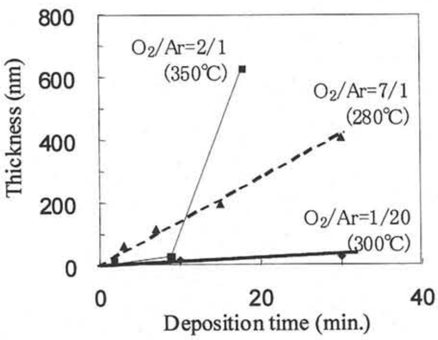

Fig. 1 Dependence of growth rates of Pt films on O_2/Ar gas ratio.

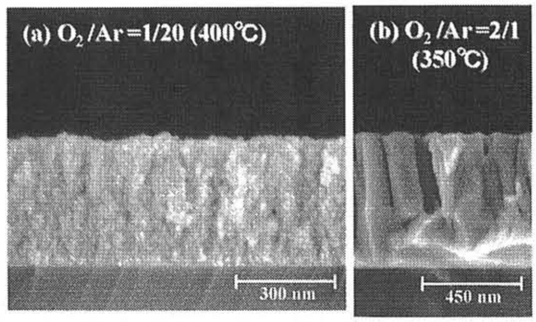

Fig. 2 Cross-sectional SEM view of Pt films deposited at O_2/Ar ratios of (a) 1/20 and (b) 2/1.

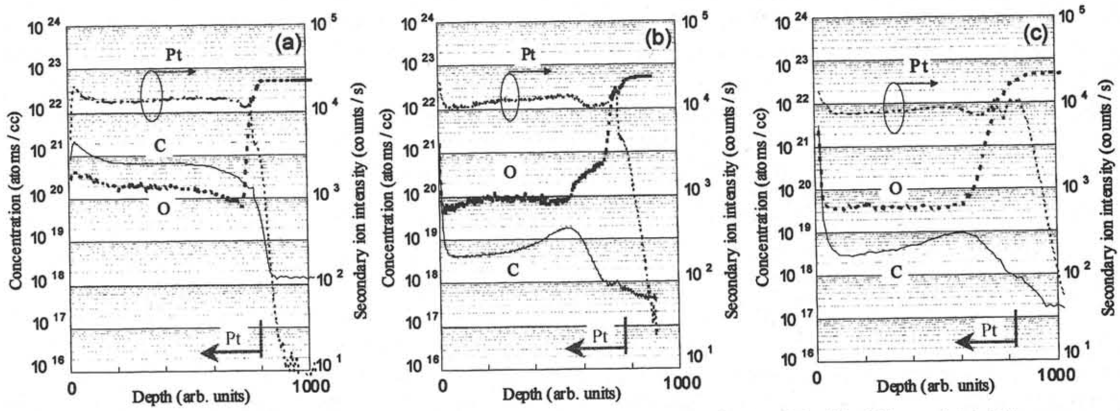

Fig. 3 SIMS profiles of Pt films deposited at O_2/Ar ratios of (a) 1/20, (b) 2/1, and (c) 7/1.

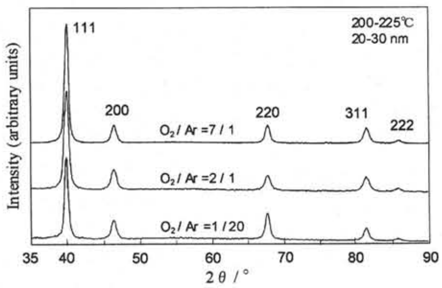

Fig. 4 Change of XRD patterns of Pt films deposited at O_2/Ar ratios of 1/20, 2/1, and 7/1.

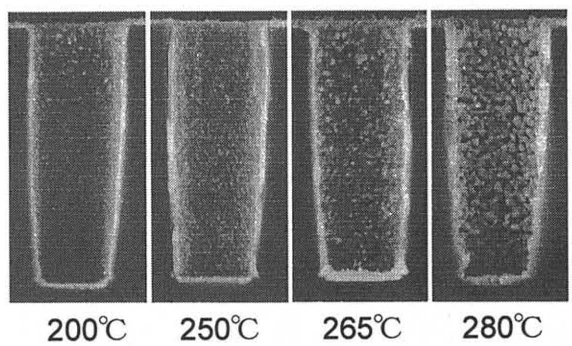

Fig. 5 Cross-sectional SEM images of Pt films deposited onto concave holes at O_2/Ar ratio of 7/1.

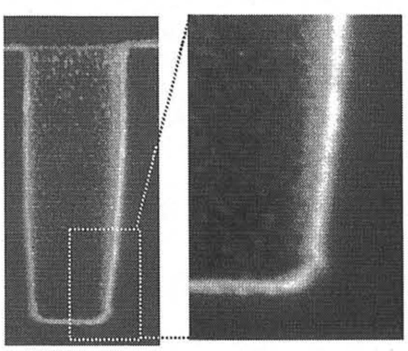

Fig. 6 Cross-sectional SEM image of Pt film deposited onto concave hole at 200°C at O_2/Ar ratio of 7/1.

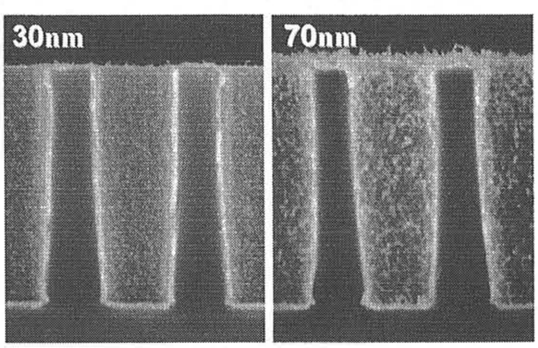

Fig. 7 Cross-sectional SEM image of Pt films with two different thicknesses deposited at 250°C at O_2/Ar ratio of 7/1.

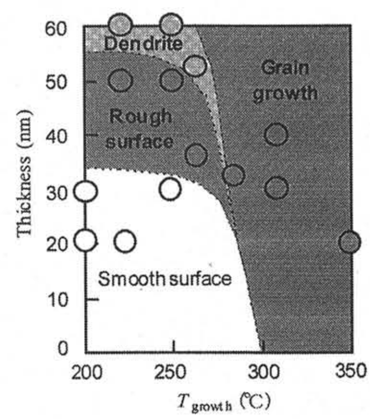

Fig. 8 Pt Film morphology as functions of film thickness and deposition temperature at O_2/Ar ratio of 7/1.