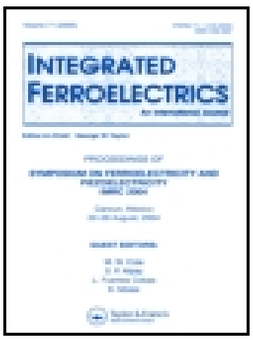

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CHARACTERIZATION OF MOCVD Pt ELECTRODE FOR FERROELECTRIC THIN FILMS

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Platinum thin films were deposited by low pressure chemical vapor deposition (LPMOCVD) on SiO_2/Si and (Ba,Sr)TiO_3/Pt/SiO_2/Si substrates using Pt-hexafluoroacetylacetonate at various deposition temperatures. The shiny mirror-like Pt thin films of a high electrical conductivity were obtained, when the deposition temperature is between 325°C and 350°C, whereas above 375°C Pt thin films showed rough surface as well as poor adhesion property to oxide substrate. Pt thin films had a good step coverage of 90%. The results indicate that LPMOCVD Pt thin films can be applied for the top electrode of high dielectric thin film, which is thought to be one of the best candidate materials for a capacitor of ULSI DRAM.

Keywords: Platinum; thin film; LPMOCVD; top electrode; ULSI DRAM

I. INTRODUCTION

Platinum (Pt) has various characteristic properties, such as an electrical conductivity, high catalytic activity, high melting point and excellent stability in an oxidizing atmosphere, which becomes a suitable conducting electrode for several materials.[1] Nowadays much attention has been paid to the Pt thin film as an electrode for high dielectric thin films, such as (Ba,Sr)TiO_3 (BST), which is one of the best candidate materials for capacitors of ultra-large scale integrated dynamic random access memory (ULSI DRAM). Especially, work function (5.5 eV) of Pt, which is larger than those of any other electrode materials, makes a high Schottky barrier with high dielectric

thin film, lowering a leakage current through the capacitor.[2] Pt is also used as a top electrode as well as a bottom electrode for symmetric electrical properties.

For 1 giga bit density DRAMs the capacitor must have a 3-dimensional stack structure with a relatively large height of the storage node and very small space between them, even though the high dielectric constant BST thin films are used as the dielectric material because of the extremely small size of the cell capacitors. Therefore, metal organic chemical vapor deposition (MOCVD) is the best way to obtain conformal deposition technique of BST thin film and top electrode.

During the last two decades various metal organic precursors of Pt have been examined, including Pt-acetylacetonate,[3,4] $Pt(PF_3)_4$,[3] cyclopentadienyl-platinum-trimethyl ($CpPtMe_3$),[5] methylcyclopentadieny-platinum-trimethyl ($MeCpPtMe_3$)[6] and Pt-hexafluoroacetylacetonate (Pt-HFA).[7] However, there are only a few reports on the MOCVD of Pt thin films for the microelectronic application. In this study, Pt thin films were deposited on SiO_2/Si, $(Ba,Sr)TiO_3/Pt/SiO_2/Si$ and patterned substrates using Pt-HFA by low pressure metal organic chemical vapor deposition (LPMOCVD), and the deposition characteristics of Pt thin films were investigated.

2. EXPERIMENTAL PROCEDURES

Platinum thin films were deposited by LPMOCVD, which consists of a vertical warm wall reactor and a resistive substrate heater and can handle wafers up to 6 inch diameter. MOCVD apparatus was shown Figure 1. Pt-hexafluoroacetylacetonate (Pt-HFA) was chosen as a metal organic precursor because of its relatively high vapor pressure and good thermal stability. Its vaporization temperature is 70°C with a vapor pressure of about 0.1 Torr, while its melting point is about 140°C.[9] Ar gas was used as a carrier gas as well as a diluent gas. The flow rate of Ar carrier gas was 100 sccm, and the total flow rate and deposition pressure were 500 sccm and 3 Torr, respectively. O_2 gas was introduced into the reactor in order to eliminate carbon incorporation into the film and to enhance decomposition of the metal organic precursor. SiO_2(1000Å)/Si, $(Ba,Sr)TiO_3$(400Å)/Pt(700Å) /SiO_2/Si and patterned SiO_2/Si wafer were used as substrates. The substrate temperature was varied from 300°C to 400°C. The deposited Pt thin films were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM) and 4-point probe.

3. RESULTS AND DISCUSSIONS

Platinum thin films are deposited on thermally grown SiO_2(1000Å)/Si at various substrate temperatures from 300°C to 400°C. Figures 2 and 3 show variation of XRD patterns and surface morphologies of Pt thin films deposited at various substrate temperatures, respectively. The deposition time and the thickness of each film were somewhat different. Those of (a), (b), (c), (d) and (e) are 30 min/100Å, 30 min/400Å, 30 min/600Å, 20 min/1000Å, and 10 min/900Å, respectively. As the deposition temperature increased, the deposition rate was increased rapidly. Since the deposition rate of the Pt thin film at 300°C was very low, its thickness was only 100 Å even for deposition time of 30 min. Moreover it did not form a continuous film

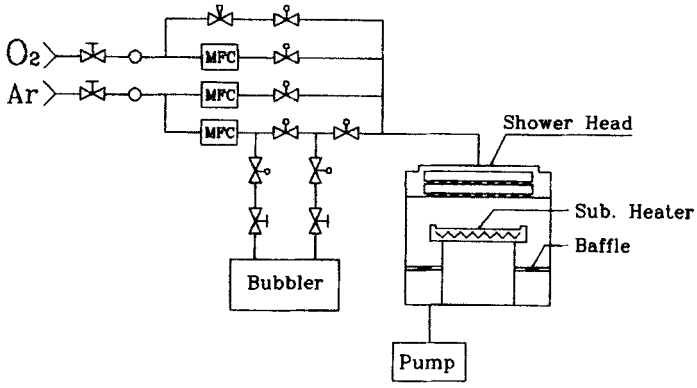

FIGURE 1 Schematic diagram of MOCVD apparatus.

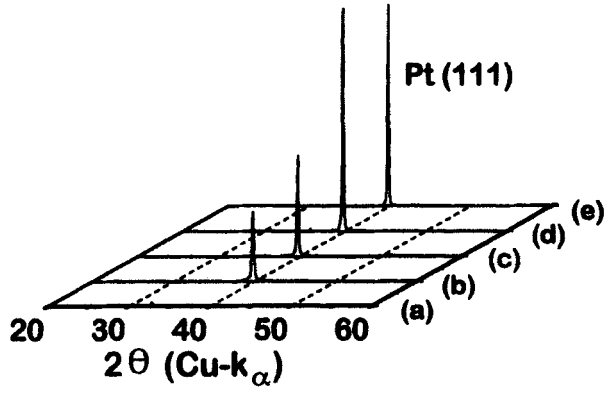

FIGURE 2 Variation of XRD patterns of Pt thin films deposited at (a) 300°C, (b) 325°C, (c) 350°C, (d) 375°C and (e) 400°C.

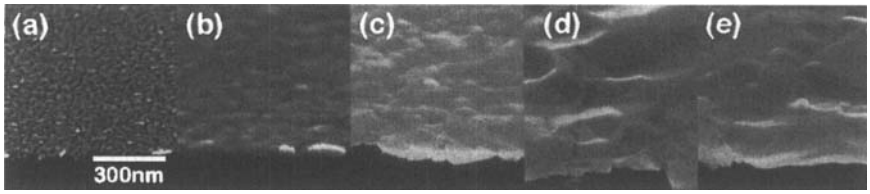

FIGURE 3 Surface morphologies of Pt thin films deposited at (a) 300°C, (b) 325°C, (c) 350°C, (d) 375°C and (e) 400°C.

because of a low surface reaction of Pt-HFA at this substrate temperature. Thus the intensity of XRD pattern was very weak. However, above a substrate temperature of 325°C, the reaction of Pt-HFA was fast enough to form continuous films and thus the intensity of Pt thin films was increased. According to the thickness and XRD peak intensity of each film, the Pt thin films deposited above 325°C appear to be completely crystallized.

All of the Pt thin films were highly oriented to $\langle 111 \rangle$ direction. The Pt thin films deposited above 375°C show only (111) peak, whereas those deposited below 350°C show very weak (200) peak at $2\theta = 46°$ in XRD patterns. Since Pt has a face centered cubic (FCC) structure, (111) plane is the densest plane and has the lowest surface energy. So the preferred growth direction of Pt thin film is $\langle 111 \rangle$.

Platinum thin films deposited above 375°C have very rough surface and milky appearance, whereas those deposited at 325°C and 350°C have relativley smooth surface morphology and shiny mirror like appearance. Moreover, the rough Pt thin films deposited above 375°C possess so poor adhesion property to oxide substrate that the Pt thin films used to peel off from the substrate during the handling. But those deposited at 325°C and 350°C has relatively good adhesion. Such a poor adhesion to oxide substrate of the Pt thin films deposited at higher temperature may be originated from a large thermal stress developed due to a large difference of thermal expansion coefficients of Pt (9×10^{-6}/K) thin film and SiO_2(4×10^{-6}/K)/Si substrate. Such a large thermal stress was also reported to be an origin of the hillock formation after heat treatment of Pt thin films.[9]

Figure 4 shows variation of resistivities of Pt thin films deposited at various deposition temperatures. As expected from the morphology of films in Figure 3, the Pt thin film deposited at 300°C had a much higher resistivity than those of other Pt thin films due to its loose microstructure. However, the continuous Pt thin films deposited above 325°C show the resistivity lower than 15μΩcm, which is comparable with the bulk resistivity

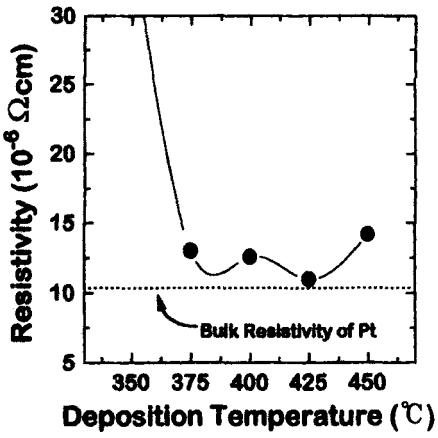

FIGURE 4 Electrical resistivities of Pt thin films deposited at various substrate temperatures.

of Pt metal of 10.8μΩcm. Therefore, the Pt thin films deposited above 325°C can be used as a top electrode for high dielectric thin films.

Figures 5 and 6 show the morphologies of Pt thin films deposited on SiO_2/Si and BST/Pt/SiO_2/Si, respectively, with changing the amount of O_2 addition. As shown in Figure 5, the amount of O_2 addition changed the morphologies of Pt thin films on SiO_2/Si substrates. Especially, with a 25 sccm O_2 flow rate, the Pt thin films did not form a continuous film. We already reported the effect of O_2 addition on the microstructure of Pt thin films on SiO_2/Si substrates in the previous study.[10] The addition of O_2 gas was essential for the deposition of Pt thin films, because no film deposition was obtained when the O_2 flow rate was zero. Smooth and dense Pt thin films, with high electrical conductivity were obtained at a flow rate above

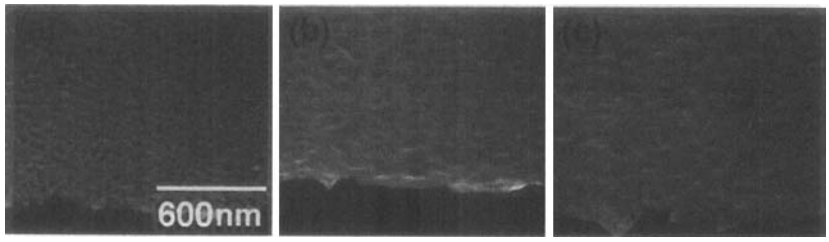

FIGURE 5 SEM micrographs of Pt thin films deposited on SiO_2/Si at 350°C with the addition of O_2 gas of (a) 25 sccm. (b) 50 sccm and (c) 100 sccm.

50 sccm O_2. The grain growth of Pt thin films during the postdeposition annealing was also suppressed as the addition of O_2 was increased during the deposition. It appears to be due to the oxidation of Pt thin film during the deposition.

However, the deposition behavior of Pt thin films on BST/Pt/SiO_2/Si substrate was somewhat different from the deposited on SiO_2/Si substrate, as shown in Figure 6. The morphology of all Pt thin films on BST/Pt /SiO_2/Si was similar regardless with the O_2 addition. The different deposition behaviour depending on substrate may be originated from either the different decomposition behaviour of Pt-HFA or the reaction between SiO_2 and HFA ligand. The deposition behaviour of Pt thin films on BST/Pt/ SiO_2/Si need to be more studied.

Figure 7 shows variation of resistivity of Pt thin films deposited on SiO_2/Si as a function of the amount of O_2 added during the deposition. The resistivity of Pt thin film deposited with the addition of 25 sccm O_2 was much higher than those of other Pt thin films because of its less dense microstructure. Figure 7 also shows the resistivity of Pt thin films annealed at 650°C for 30 min in air atmosphere. The higher resistivity of Pt thin films deposited at 25 sccm O_2 was due to a severe agglomeration of grains which resulted in the formation of large holes in the Pt thin films.[10] However, the Pt thin films deposited above 50 sccm O_2 did not show any change of resistivities after postannealing.

A conformal deposition of Pt thin films on the patterned SiO_2/Si substrate is shown in Figure 8. Pt thin films were deposited at 350°C. Pt thin film was well deposited in a trench with about 3000Å of space, showing a step coverage of above 90%. The actual space between the storage nodes in 1 giga bit density ULSI DRAM may be smaller than 1000Å. However, the conformal deposition of Pt thin films in 3000Å space suggests that the thermal LPMOCVD technique might be applied in 1Gb ULSI DRAM capacitor process.

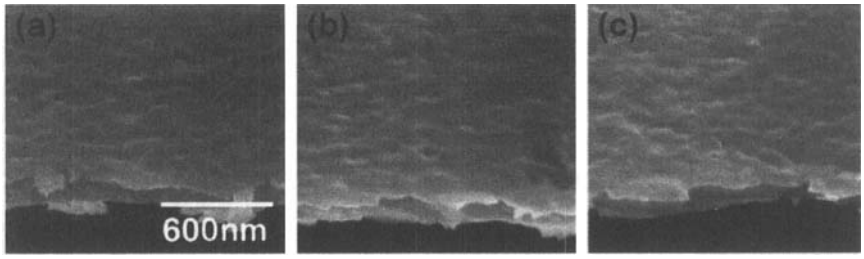

FIGURE 6 SEM micrographs of Pt thin films deposited on BST/Pt/SiO_2/Si at 350°C with the addition of O_2 gas of (a) 25 sccm, (b) 50 sccm and (c) 100 sccm.

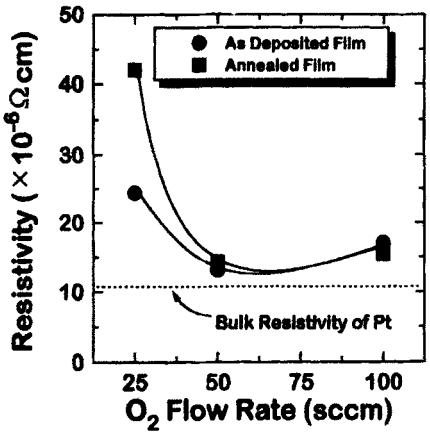

FIGURE 7 Electrical resistivities of Pt thin films deposited with the addition of various amount of O_2 during the deposition.

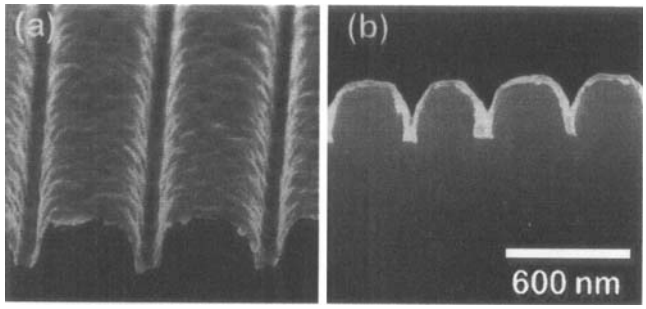

FIGURE 8 SEM micrograph of Pt thin films deposited on patterned SiO_2/Si at 350°C : (a) top view and (b) cross-sectional view.

4. CONCLUSIONS

Platinum thin films were deposited on SiO_2/Si and $BST/Pt/SiO_2/Si$ substrates by LPMOCVD at various substrate temperatures between 300°C and 400°C. As the substrate temperature increased, the deposition rate was rapidly increased. However, above 375°C the surface roughness increased and the adhesion property to oxide substrate became worse. In an optimum substrate temperature range between 325°C and 350°C, Pt thin films show low electrical resistivity below 15μΩcm and shiny mirror-like appearance. Pt thin films had a good step coverage of above 90% for the trench of 3000Å space. In conclusion, Pt thin films deposited by the LPMOCVD technique appears to be suitable to a top electrode for high dielectric thin film, which can be used as a capacitor in 1Gb ULSI DRAM.

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