

# Deposition of Platinum Thin Films for the Electrodes of FeRAMs in Supercritical Carbon Dioxide

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## Abstract

Platinum thin films were deposited onto planar and trench structure SiO<sub>2</sub>/Si substrates by using supercritical fluid deposition (SCFD). In SCFD, H<sub>2</sub> was often used as reducing agent. However, Pt films could not be deposited by H<sub>2</sub> reduction, while reduction by cyclohexane enables to obtain continuous Pt films with carbon impurities. To remove carbon in Pt films, we employed post deposition annealing (PDA) under O<sub>2</sub> atmosphere and obtained pure Pt films which do not contain any carbon.

## 1. Introduction

As device size of ULSI shrinks, the size of memory capacitors has been shrinking. To maintain the capacitance of memory capacitors, it is necessary that surface area of capacitors is not reduced even though capacitor projected area decreases. Thus, capacitor structure will become more complicated like as a trench features. Thus, ultra-thin and conformal capacitor electrodes will be required and Pt is one of the major candidates for electrodes of memory capacitor such as ferroelectric random access memories (FeRAMs).

To fabricate conformal films, we applied SCFD method. In SCFD, supercritical CO<sub>2</sub> (scCO<sub>2</sub>) is used as solvent and deposition is performed by chemical reactions of precursors in scCO<sub>2</sub>. Several metal depositions such as Cu, Ag, and Au by SCFD have already been reported [1-3]. In this work, we tried to deposit Pt thin films for electrodes of FeRAMs by SCFD.

## 2. Experimental

Pt thin films were deposited on planar Si substrate with thermal SiO<sub>2</sub> (100nm) and trench structure with thermal SiO<sub>2</sub> (20nm) in scCO<sub>2</sub>. To deposit Pt films, we used dimethyl(1,5-cyclooctadiene) platinum (II) (PtMe<sub>2</sub>COD) as precursors. H<sub>2</sub> and cyclohexane were used as reducing agent. Experimental equipment is shown in Fig.1.

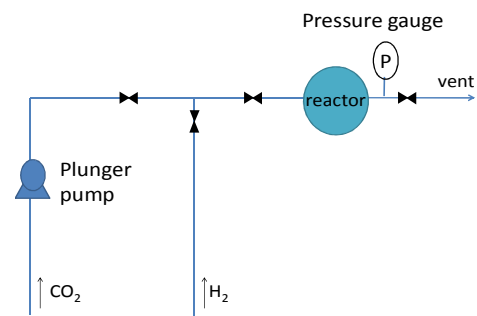


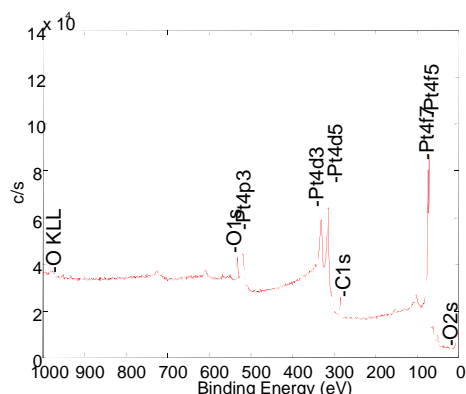
Figure 1 Experimental equipment.

Deposition was performed in a hot-wall reactor. Substrates were placed in the reactor with precursors. Reactor was filled with CO<sub>2</sub> to 8MPa at 50°C by using plunger pump. Then, substrate was heated up to 250°C and kept at this temperature for 60 min. Deposited film composition was evaluated by X-ray photoelectron spectroscopy (XPS), film thickness profile in the trench was monitored by using field emission scanning electron microscope (FE-SEM), and surface morphology of films was studied by atomic force microscope (AFM).

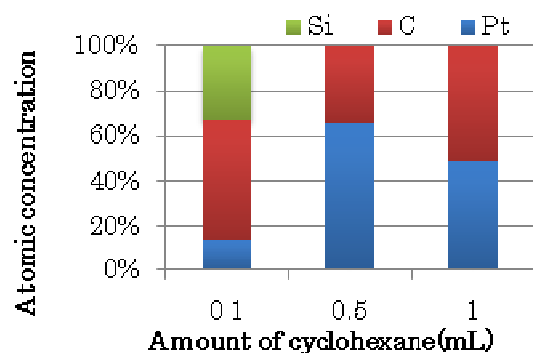
## 3. Results and discussion

We tried to deposit Pt films by using PtMe<sub>2</sub>COD as precursor and H<sub>2</sub> as reducing

agent. By H<sub>2</sub> reduction, we could not yield continuous Pt films. Then, we used cyclohexane as reducing agent. Cyclohexane decomposes to benzene and H<sub>2</sub> with the assist of Pt catalysis. In this case, Pt acts as auto-catalysis and promotes decomposition of cyclohexane. Compared to H<sub>2</sub>, cyclohexane can be supplied in high concentration because it is liquid. Moreover, cyclohexane gives six hydrogen atoms, while H<sub>2</sub> gives two. Thus, cyclohexane may be a promising reducing agent in Pt deposition. Figure 2 shows XPS spectrum of Pt film that was deposited by using cyclohexane as reducing agent.



**Figure 2** XPS spectrum of Pt film deposited by using cyclohexane as reducing agent.

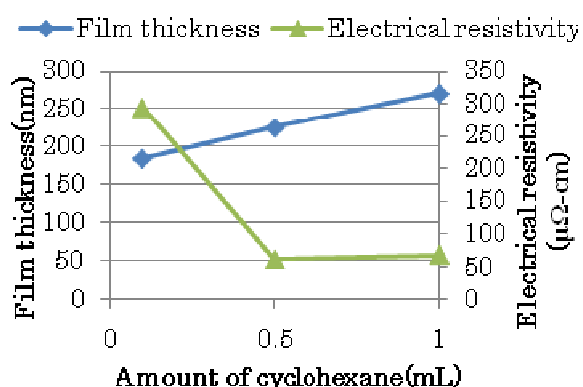


**Figure 3** Atomic concentration of Pt films deposited by a various amount of cyclohexane.

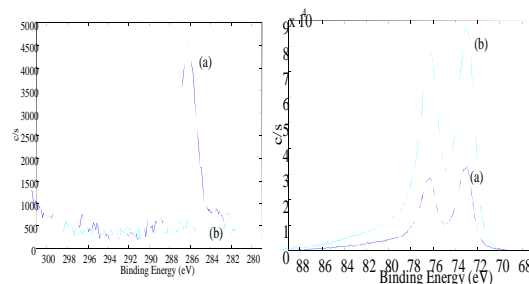
There is no peak of Si, which suggests deposited Pt film is continuous. C peak appears, however, strongly and electrical resistivity of the film was 52 $\mu\Omega$ -cm. Figure

3 shows the relationship of atomic concentration of films and the amount of cyclohexane.

Figure 4 shows the relationship of electrical resistivity and film thickness against the amount of cyclohexane. Then we tried to remove carbon in Pt films by PDA. PDA was performed at 400 °C and annealing atmospheres were vacuum and O<sub>2</sub> gas (100Torr). The results of PDA are shown in Fig.5.

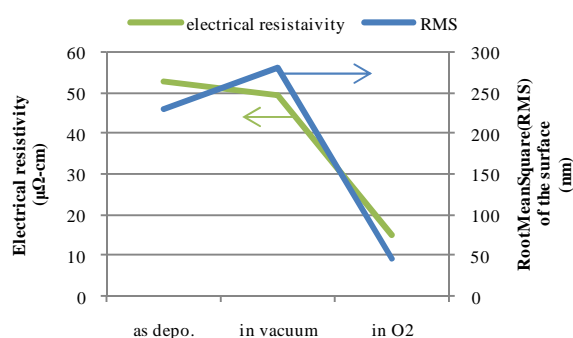


**Figure 4** The relationship between the amount of cyclohexane and the film thickness and electrical resistivity of Pt films.



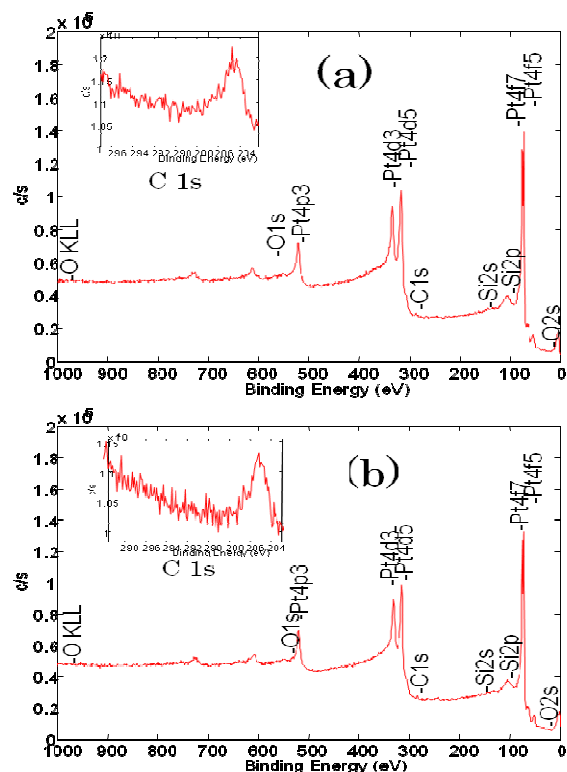
**Figure 5** C 1s (left) and Pt 4f (right) peaks of Pt films after PDA at 400 °C under (a) vacuum and (b) O<sub>2</sub> gas.

By PDA in vacuum, carbon in Pt films was almost the same as before PDA and carbon content of film after PDA in vacuum was 25%, while by PDA in O<sub>2</sub> gas, carbon in Pt films was completely removed as shown in Fig.5. The resistivity of Pt film after O<sub>2</sub>-PDA decreased to 15 $\mu\Omega$ -cm and surface morphology of the films was improved as shown in Fig.6.



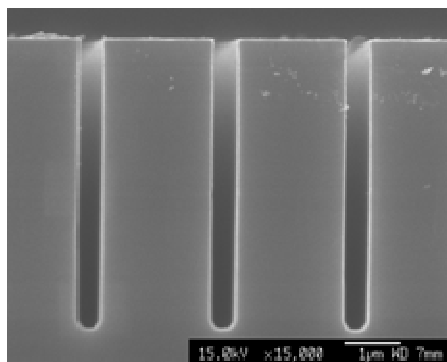
**Figure 6** The transformation of Pt films through annealing.

When the PDA temperature was lower than 400 °C, carbon in Pt films were not completely removed as shown in Fig.7.



**Figure 7** XPS spectra of Pt films after PDA at (a) 300 °C and (b) 350 °C.

Pt deposition into trench structures was also performed by using cyclohexane as reducing agent. Figure 8 shows good step coverage of Pt film (95%).



**Figure 8** Pt deposition into trench structures.

#### 4. Conclusion

In Pt deposition by SCFD, H<sub>2</sub> reduction could not yield continuous films. Using cyclohexane as reducing agent, continuous Pt films were obtained. Pt films deposited by cyclohexane, however, contained much carbon. Carbon in Pt films was completely removed by PDA with O<sub>2</sub> gas. Pt films deposited into trench structures showed conformal step coverage. Thus, Pt deposition by SCFD have capability to fabricate the electrodes of FeRAMs.

#### 5. References

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