



Ruthenium Bottom Electrode Prepared by Electroplating for a High Density DRAM Capacitor

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The possibility of Ru electroplating for application as the bottom electrode in high density dynamic random access memory (DRAM) capacitors was investigated. Prior to Ru electroplating on a TiN substrate, HF cleaning and Pd activation were performed. Removal of Ti oxide from the TiN substrate by HF treatment enabled Pd activation, which enhanced the nucleation of Ru on TiN substrate. Optimized pretreatments led to a continuous Ru film deposition. The surface roughness was measured to be 4.4 nm at 45 nm Ru film on the bare substrate. Moreover Ru electroplating method was also applied to a capacitor node-type TiN wafer. The deposition rate of Ru on the patterned wafer was the same as that on a bare wafer. The film showed 93% step coverage and good adhesion, comparable to CVD Ru films.

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As the device density of dynamic random access memory (DRAM) increases to gigabyte scale, the unit cell size, consisting of one transistor and one capacitor, decreases to $0.1 \mu\text{m}^2$. As unit cell size decreases, the fabrication of 25 fF capacitor has become a central issue in DRAM manufacturing. In the gigabit density era, the use of new materials with high dielectric constants (ϵ) such as Ta_2O_5 and $(\text{Ba}, \text{Sr})\text{TiO}_3$ has been proposed as a new solution.^{1,2} In high dielectric material integration, a bottom electrode with high oxidation resistance and high work function is required. As the suitable metals which satisfy above two requirements, Pt,^{3,4} Pt/Ru, and Ru were proposed.

Among these metals, Pt has been used as a bottom electrode. But oxygen diffusion and bad etching property have become problems in deep submicrometer dimension era. Alternatively, Ru film has recently attracted attention as a substitution of Pt because it can be easily patterned, has good etching property and forms oxygen diffusion preventing layer of RuO_2 on top of Ru film during high ϵ material deposition. Pt/Ru is also considered to be suitable as a bottom electrode due to high work function and oxygen diffusion preventing layer of RuO_2 at interface between Pt and Ru. In spite of these advantages, it cannot be applied to deep submicrometer dimension era because it is too thick to apply to deep submicrometer dimension structure. From above description it can be concluded that Ru is the most promising material.⁵⁻⁸

Chemical vapor deposition (CVD)^{8,9} and physical vapor deposition (PVD)¹⁰ have been widely used for the deposition of Ru films. These two processes have certain limitations including narrow process window, complex apparatuses, and high cost. In addition, rough surface morphology and poor step coverage are becoming important obstacles as feature size shrinks. Electroplating represents an alternative for the deposition of thin metal films because of good film quality, simple apparatus, and its low cost. In spite of these advantages, however, electroplating has rarely been used for depositing Ru film on semiconductor devices.¹¹⁻¹⁷ The chief problems of Ru electroplating on a TiN substrate are Ru nucleation and limitation on the current distribution associated with high resistivity of the TiN barrier layer.¹⁸⁻²⁰

In this study, Pd activation was investigated as a nucleus formation method to make Ru electroplating possible on TiN substrate. The size and density of nuclei were optimized, and Ru electroplating was carried out onto Pd activated TiN substrate. Then the quality of Ru film was estimated.

Experimental

The substrates used in this study were CVD TiN (10 nm)/PVD Ti (15 nm)/Si (100) blanket wafers and CVD TiN (20 nm)/Si (50 nm)/ SiO_2 patterned wafers (aspect ratio 2.5:1).

Prior to electroplating, two surface pretreatments on TiN substrate were performed sequentially. Ti oxide was removed from TiN substrate by using 1% HF solution for 10 min followed by deionized (DI) water cleaning. Pd activation was done in the Pd activation solution of pH 2.57 composed of PdCl_2 , 50% HF (12.5 mL/L), and HCl (3.0 mL/L) while PdCl_2 concentrations were varied from 0 to 0.4 g/L. The oxide free TiN substrate was dipped in Pd activation solution for 20 s and rinsed with DI water.

After pretreatment process, Ru electroplating was performed. Ru source and adjusting salt were W-RU2 (Japan Energy). The Ru electrolyte was made up of ruthenium sulfate solution (5 g/L), NaOH (40 g/L), and adjusting salt (100 g/L). The adjusting salt was composed of phosphoric acid, sulfamic acid, and ammonium sulfamate. The pH of Ru electrolyte was 1.3. A constant -1.3 V potential was applied by a PAR 263 (EG&G Princeton Applied Research Corporation) with respect to saturated calomel electrode (SCE) at room temperature. And the current density was 42 mA/cm^2 with this applied potential. Electroplating was carried out on both bare wafer and patterned wafer at the same condition.

The Ru film was characterized using field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) measurement, atomic force microscopy (AFM), and Auger electron spectroscopy (AES). The resistivity of ruthenium film was measured using the standard four-point-probe method.

Results and Discussion

To find out an optimum Pd activation condition, PdCl_2 concentrations were varied from 0.025 to 0.4 g/L. The deposited Pd particles were analyzed by XPS and FESEM as shown in Fig. 1 and Fig. 2. Both Pd and PdCl_2 were found on the activated TiN substrate.

According to AFM analyses, the size of the Pd particle increased in proportion to PdCl_2 concentration. It was smaller than 5 nm below 0.025 g/L PdCl_2 concentration, and larger than 10 nm above 0.4 g/L PdCl_2 concentration. Pd densities were almost same to be $8.25 \times 10^{10}/\text{cm}^2$, independent of PdCl_2 concentration of 0 to 0.4 g/L at 1% HF concentration. Figure 3a to 3e show the difference in density due to the shading of large particles over small ones. Among different PdCl_2 concentrations, Pd activation with 0.1 g/L PdCl_2 showed the most uniform size distribution and the smallest surface roughness of 2.9 nm as shown in Fig. 2 and 3c.

For variable Pd activation conditions Ru electroplating was performed on TiN substrate as shown in Fig. 4. Below the concentra-

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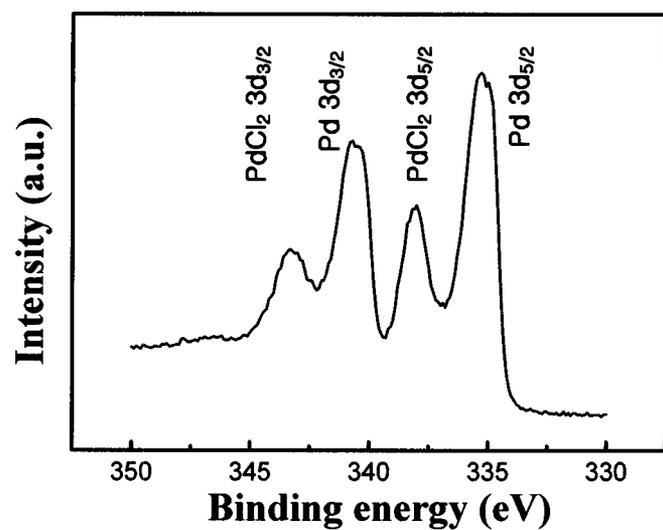


Figure 1. XPS spectrum of TiN substrate activated with 0.1 g/L PdCl₂.

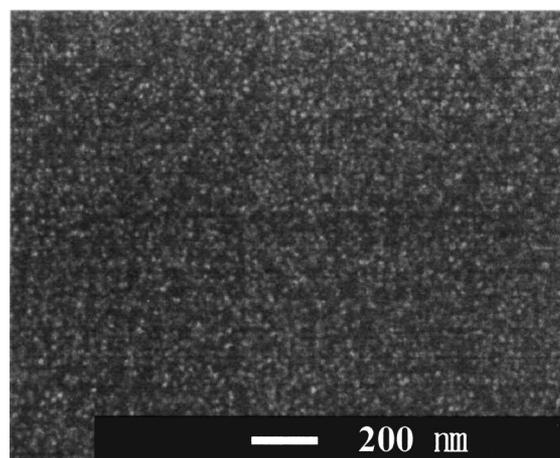


Figure 2. Surface FESEM image of TiN substrate activated with 0.1 g/L PdCl₂.

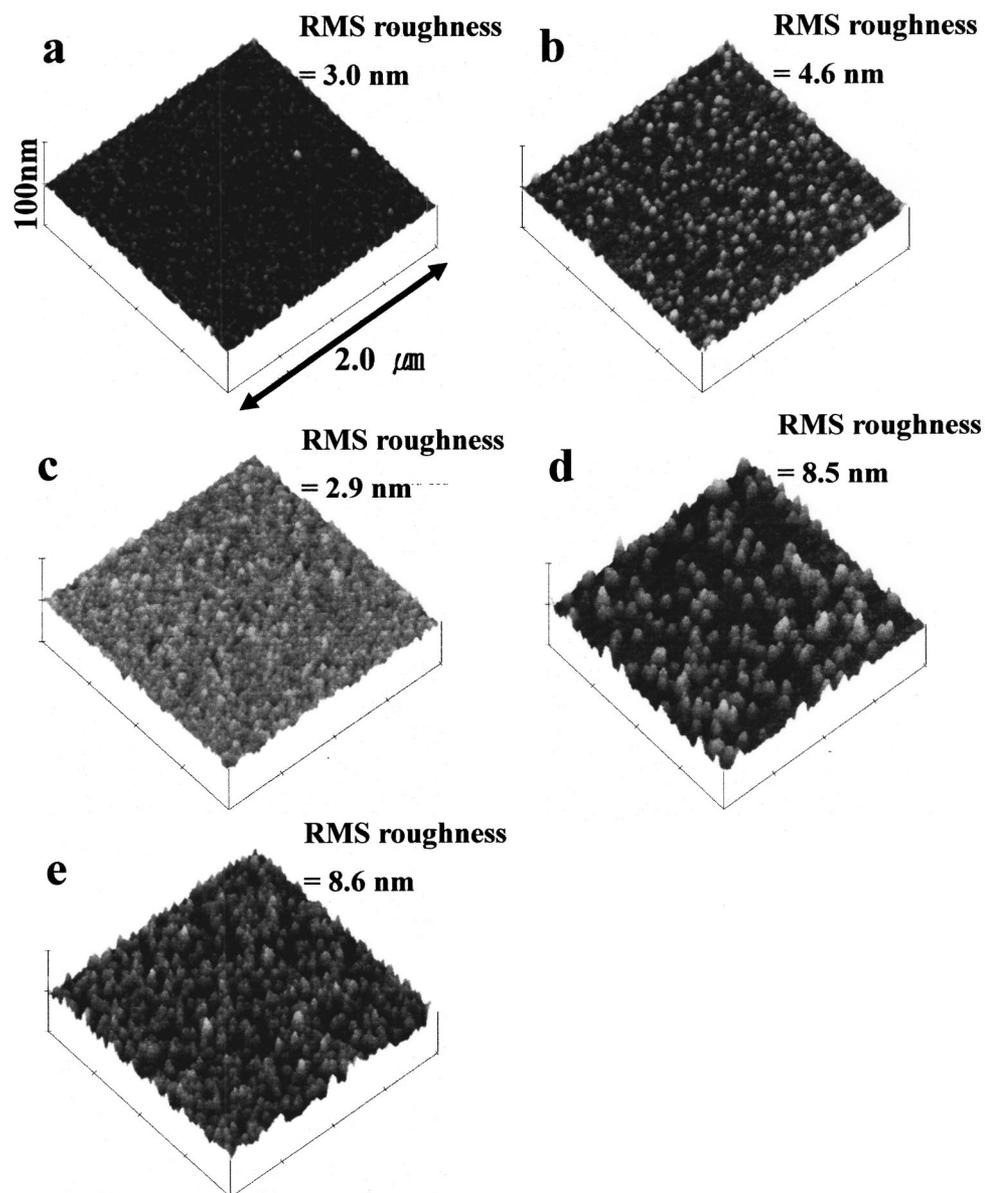


Figure 3. AFM analyses of TiN substrate activated with different PdCl₂ concentrations (a) 0.025 g/L, (b) 0.05 g/L, (c) 0.1 g/L, (d) 0.2 g/L, and (e) 0.4 g/L.

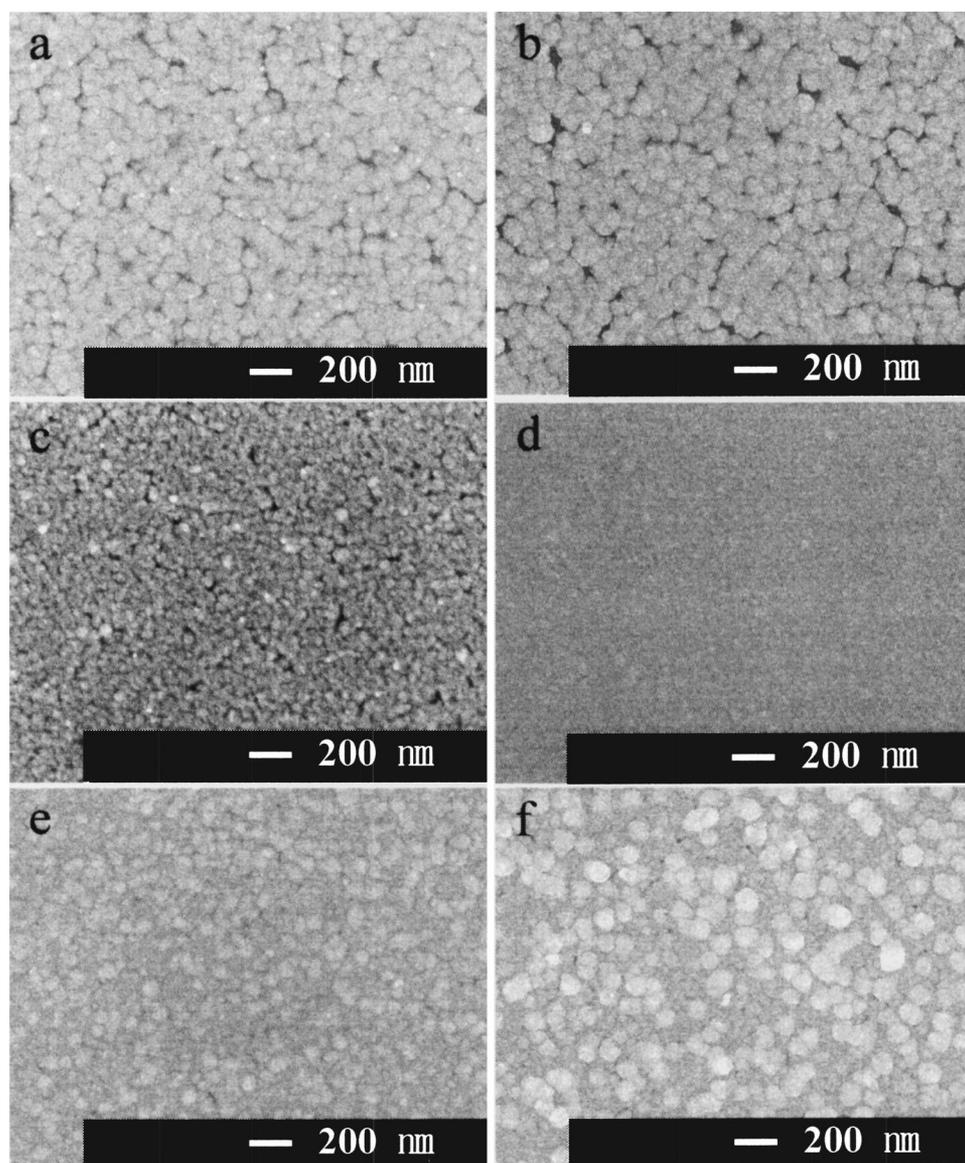


Figure 4. Surface FESEM images of Ru film activated with PdCl₂ concentration of (a) 0 g/L, (b) 0.025 g/L, (c) 0.05 g/L, (d) 0.1 g/L, (e) 0.2 g/L, and (f) 0.4 g/L.

tion of 0.1 g/L PdCl₂, the Ru film was not continuous and in the range of 0 to 0.025 g/L PdCl₂, Ru cluster size and surface morphology were almost identical. These phenomena reveal that Pd particles below 5 nm do not work as the nucleation centers. In the range of 0.05 to 0.1 g/L PdCl₂ concentration, Ru clusters became smaller and a continuous Ru film was obtained. However, for Ru films activated above 0.2 g/L PdCl₂ concentration, the Ru clusters were larger and the surface morphology was rougher compared with films activated in solution with 0.05 to 0.1 g/L PdCl₂. This is ascribed to the larger Pd particle size associated with the 0.2 g/L PdCl₂ (Fig. 4e and f). These observations indicate that there is an optimum PdCl₂ concentration for making Ru film continuous and smooth. A near optimum 5 nm Pd particle size was obtained in a 0.1 g/L PdCl₂ at 1% HF solution. The thickness and surface morphology of a Ru film deposited from a 0.1 g/L PdCl₂ solution are shown in Fig. 5a and b. Film thickness was 45 nm and root mean square (rms) surface roughness was 4.4 nm. The RMS surface roughness was below 10% of Ru film thickness and which enabled application as a bottom electrode of a DRAM capacitor. And the adhesion of Ru film was tested with American Society for Testing and Materials (ASTM) tape test method. Ru film was not peeled off by tape test method.

To investigate the compositional characteristics and crystalline structures of Ru film, AES, XPS and XRD analyses were performed. Carbon contamination was checked by using low intense Ru (MNN) peak because high intense Ru (MNN) peak overlaps with carbon (KLL) peak in AES analysis and by comparing the area ratio of Ru/RuO₂ of 3d_{5/2} peak with that of 3d_{3/2} peak in XPS analysis. Carbon was not detected in both analysis methods. In the AES analysis, it is found that some oxygen is contained in the Ru film and Pd particles exist at the interface of Ru and TiN (Fig. 6a). It can be inferred from Fig. 6b that the oxygen content in the Ru film corresponds to RuO₂. Four overlapping peaks at 280.0, 280.7, 284.2, and 284.7 eV were observed in XPS data. Among them, 280.0 and 284.2 eV correspond to the 3d_{5/2} and 3d_{3/2} binding energy of Ru, and 280.7 and 284.7 eV indicate the 3d_{5/2} and 3d_{3/2} binding energy of RuO₂. Moreover, XRD analysis points out that RuO₂ is amorphous (Fig. 7), in which a weak and broad peak around 35.16° reveals RuO₂. Therefore it can be concluded that the electroplated Ru film is the composite film of Ru and RuO₂. The ratio of RuO₂ to Ru is 1/24 in the middle of as-deposited film, which was calculated with AES data by considering sensitivity factor and stoichiometric number. And the ratio of Ru/RuO₂ (1/3 in AES analysis and 1/2 in

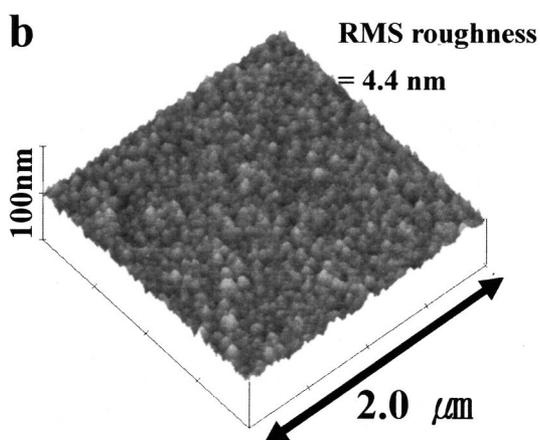
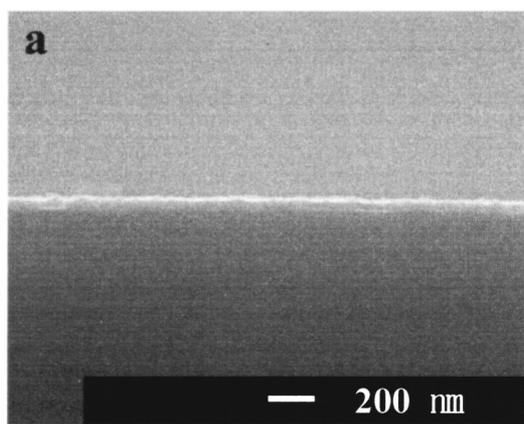


Figure 5. (a) Cross sectional FESEM image of Ru film activated with 0.1 g/L PdCl₂, and (b) AFM analysis of Ru film activated with 0.1 g/L PdCl₂.

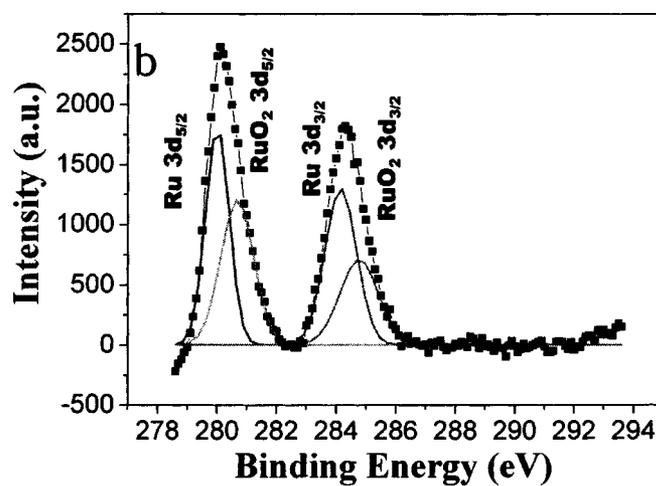
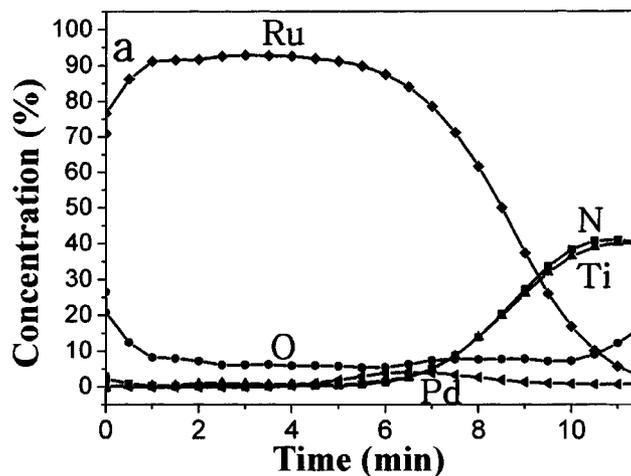


Figure 6. (a) AES depth profile of Ru film activated with 0.1 g/L PdCl₂ and (b) XPS spectrum of Ru film activated with 0.1 g/L PdCl₂.

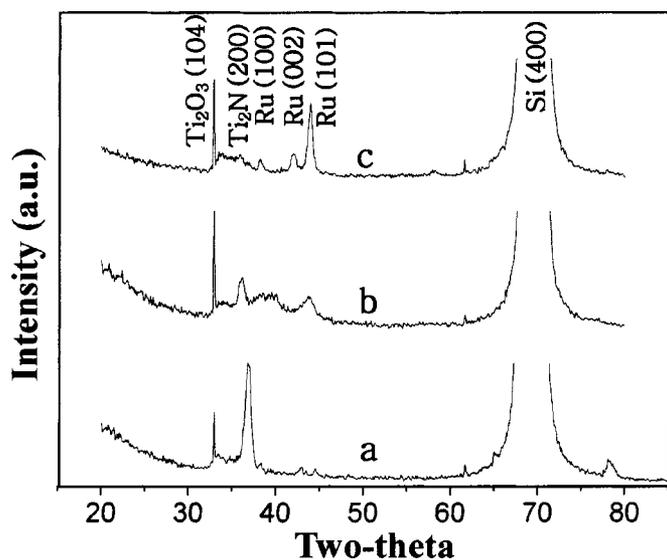


Figure 7. XRD patterns of (a) TiN substrate, (b) Ru film after electroplating, and (c) Ru film after anneal process at 500°C for 10 min in air atmosphere.

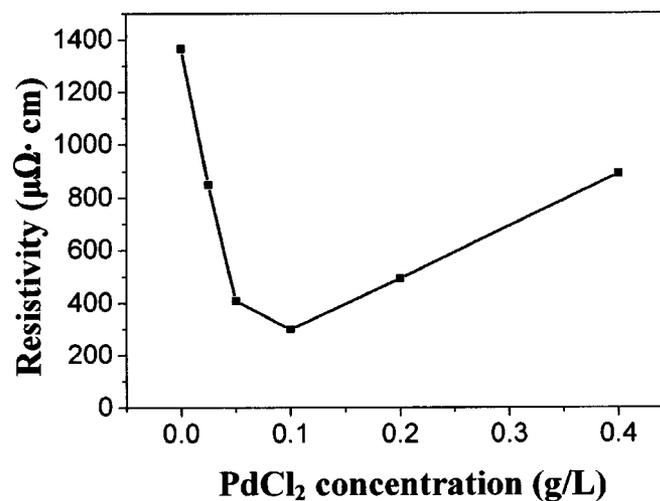


Figure 8. Trend of resistivity of electrodeposited Ru film.

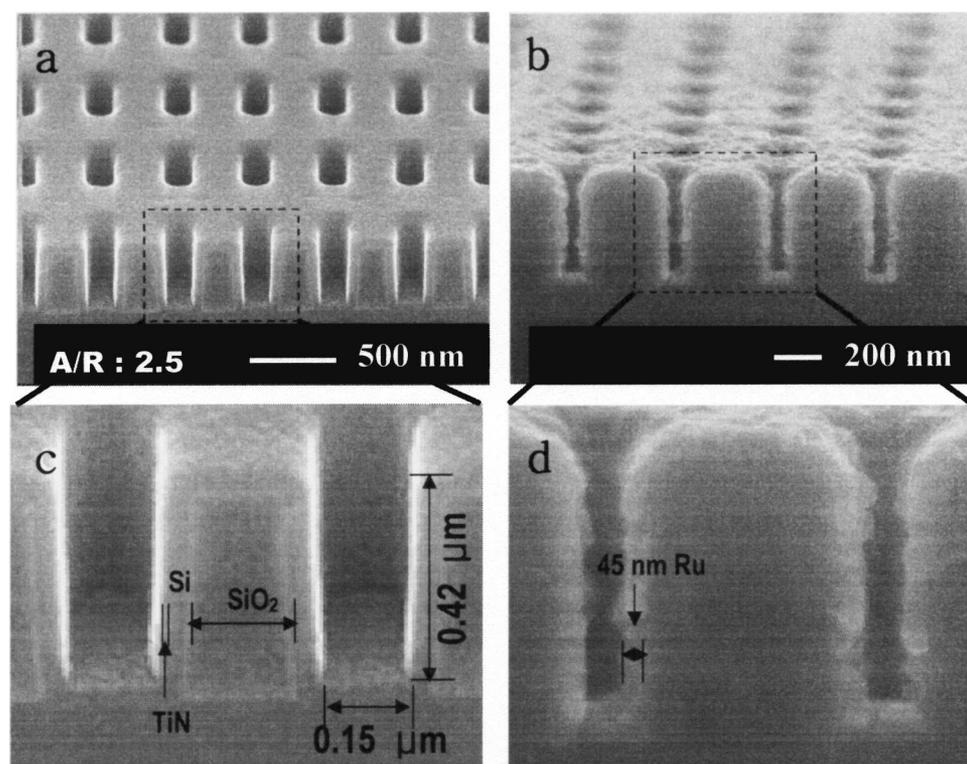


Figure 9. FESEM micrographs of (a) patterned TiN wafer, (b) Ru film on patterned TiN wafer, (c) patterned TiN wafer (enlarged), and (d) Ru film on patterned TiN wafer (enlarged).

XPS analysis) is lower at the surface than in the middle of film due to native oxide. Inclusion of oxygen into the middle of film is hard to be avoided in solution experiment due to high affinity of Ru to oxygen.^{21,22} Thus to remove oxygen content from Ru film, post-treatment such as electrical reduction and anneal were suggested and showed possibility. These processes are to be studied.

As-deposited Ru film showed small cluster size and poor crystalline structure by XRD pattern in Fig. 7b. But after anneal process at 500°C for 10 min in air, (101) preferred orientation was obtained and (100), (002) peaks appeared during anneal because of grain growth and recrystallization. By comparing Fig. 7a with 7b, it can be seen that a Ti₂N (200) peak shifted to the left after annealing, so that compressive stress is applied to Ru film.

The trend of resistivity of Ru film is shown in Fig. 8. The resistivity of 300 μΩ cm of as-deposited Ru film in Ru film deposited by electroplating is relatively higher than that of metallorganic CVD (MOCVD) Ru film. It is believed that small cluster size, poor crystalline structure and impregnated amorphous RuO₂ contribute to the high resistivity. With annealing process, however, this high resistivity of Ru film can be further reduced to 38 μΩ cm due to grain growth and recrystallization of Ru, which is comparable to the resistivity of MOCVD Ru film. Oxidation of Ru in the film did not occur during annealing because thin RuO₂ layer formed on top of the film prevented further diffusion of oxygen.³

The optimized process condition of Ru electroplating onto bare wafer was applied on capacitor node-type TiN patterned wafer to examine the possibility of Ru electroplating to real DRAM fabrication method. The minimum feature size of TiN wafer used in this study was 0.15 μm with 2.5:1 aspect ratio, and the structure of substrate was CVD TiN (20 nm)/Si (50 nm)/SiO₂ as shown in Fig. 9. The experimental conditions including 0.1 g/L PdCl₂ activation were the same as those in the bare wafer experiment. In patterned wafer, the film thickness was about 45 nm, which is the desired node thickness to 0.1 μm² cell size DRAM application with the consideration of the thickness of Ta₂O₅ and it of top electrode. And the deposition rate was 7.5 nm/min, which is the same value in the bare wafers. The pattern was well covered with Ru film throughout a

wafer, showing 93% step coverage and smooth surface morphology. And it also showed good adhesion.

Conclusion

The possibility of Ru electroplating for application as the bottom electrode fabrication method of a high-density DRAM capacitor was investigated. Without the Pd activation process, a discontinuous Ru film was obtained due to the low density of nucleation center. But after Pd activation was performed with 0.1 g/L PdCl₂ for 20 s on TiN wafer, a continuous Ru thin film was obtained. After electroplating, the Ru film had 45 nm thickness, 7.5 nm/min deposition rate, and 4.4 nm surface roughness. These are appropriate value for DRAM application. The resistivity of electroplated Ru film was high compared with that of MOCVD Ru film, but it could be further reduced by annealing. A reduced resistivity of 38 μΩ cm was obtained although the optimal annealing conditions have not been established. With a capacitor node-type wafer, Ru electroplating also showed the same thickness as bare TiN wafer, acceptable surface roughness, 93% step coverage, and good adhesion. These results indicate that Ru electroplating is comparable to Ru MOCVD method.

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