

C-1-5

## Plasma-Enhanced ALD Ru Thin Films on PVD-TaN Films with Smooth Morphology at Low Temperature Using DER Ru Precursor

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### Introduction

Ruthenium (Ru) is one of promising candidates as a seed layer material, because its resistivity is lower than the conventional Ta-based barrier materials and it realizes seedless Cu electrochemical deposition (ECD) [1]. For void-free Cu interconnects, the conformal seed layer deposition in the damascene structure is strongly required. Atomic layer deposition (ALD) method is a possible solution to overcome this issue. We have reported the plasma-enhanced (PE) ALD of Ru thin films on WNC barrier films using bis(ethylcyclopentadienyl)ruthenium [Ru(C<sub>2</sub>H<sub>5</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>; Ru(EtCp)<sub>2</sub>] with NH<sub>3</sub> plasma as reducing agent for the Ru precursor, previously [1]. In a sequential work, we examined the Ru film deposition on conventional PVD-TaN barrier films by the PE-ALD using Ru(EtCp)<sub>2</sub>. The surface morphology of the obtained Ru film was rougher than that on WNC. The temperature of 400 C is required to obtain adequate deposition rate for Ru(EtCp)<sub>2</sub> precursor. This high temperature causes the surface roughness.

In this work, for deposition of the Ru films with smooth surface morphology on TaN films, we examined (2, 4- dimethylpentadienyl)(ethylcyclopentadienyl)Ru (DER) as Ru precursor. The temperature required by Ru film deposition will be decreased using DER to realize the deposition with smooth surface morphology at adequate deposition rate.

### Experimental

Ruthenium films were deposited on 5 nm thick PVD-TaN/100nm thick SiO<sub>2</sub>/Si wafers. A cycle of Ru deposition process composed of Ru precursor pulse feed-purge-NH<sub>3</sub> gas pulse feed (including plasma ignition)-purge (Fig.1).

Ru films were deposited at the stage temperatures of 300 C–400C. Ru precursors were carried into the reactor

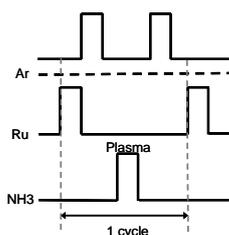


Fig.1 PEALD-Ru gas sequence.

chamber using Ar carrier gas by bubbling feed system. The Ru films characteristics were measured using four-point probe method, x-ray reflection (XRR), and transmission electron microscopy (TEM).

### Results and Discussion

The dependence of the Ru films thickness after 300 deposition cycles on the stage temperatures are shown in Fig. 2a. The deposited film thickness per deposition cycle using DER was thicker than that using Ru(EtCp)<sub>2</sub>. For both DER and Ru(EtCp)<sub>2</sub> precursors, the deposited film thickness per deposition cycle increased with the wafer temperature. The density of the deposited Ru films using DER precursor was constant regardless of the stage temperature (Fig. 2b). However, the film density using Ru(EtCp)<sub>2</sub> was slightly lower than that using DER at the 300 C wafer temperature (Fig. 2b). The TEM images of the films after 300 deposition cycles at 300 C stage temperature are shown in Fig. 3. The film surface

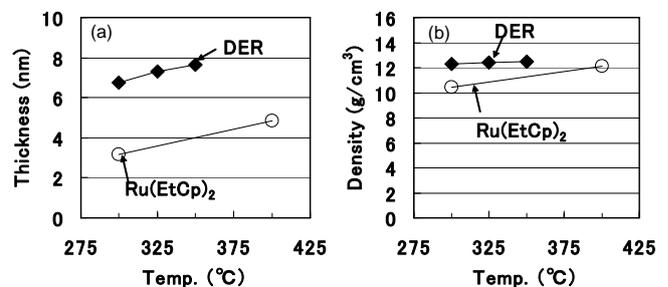


Fig.2. Stage temperature dependence of (a) Thickness, (b) Density.

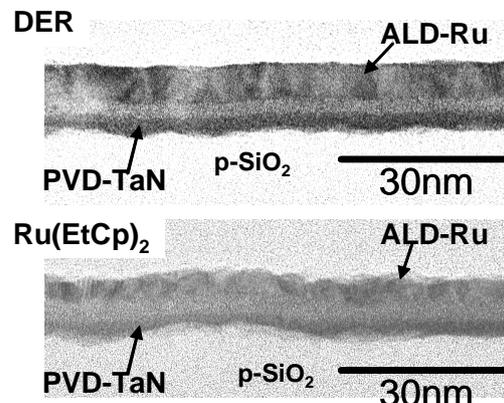


Fig.3 TEM image of Ru films using DER and Ru(EtCp)<sub>2</sub>

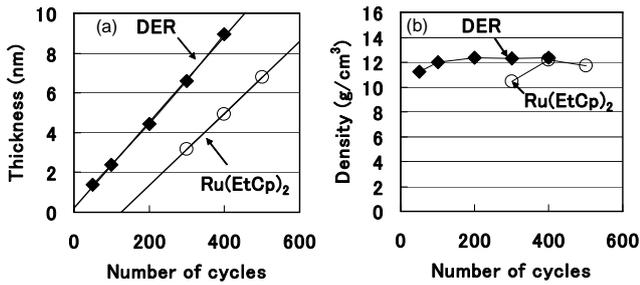


Fig. 4. Number of cycles dependence of (a) Thickness, (b) Density.

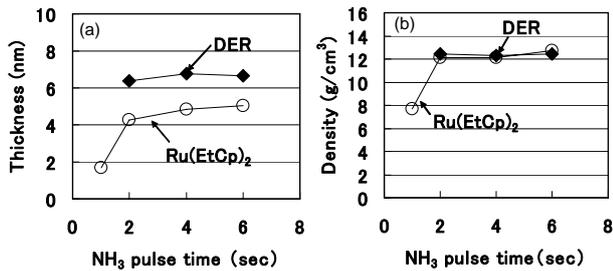


Fig. 5. NH<sub>3</sub> pulse time dependence of (a) Thickness, (b) Density.

morphology deposited using DER precursor was smoother than that using Ru(EtCp)<sub>2</sub>. It is reported that the Ru nuclei generation rate of thermal chemical vapor deposition of Ru using DER is higher than that using Ru(EtCp)<sub>2</sub> because of the lower decomposition temperature of DER [2]. The molecular structure of DER is speculated to be less stable under NH<sub>3</sub> plasma than that of Ru(EtCp)<sub>2</sub>. Therefore, it is considered that the smooth Ru surface using DER was caused by their higher nuclei generation rate due to the less stability of DER under plasma. The difference in the Ru nuclei generation rate between DER and Ru(EtCp)<sub>2</sub> was reflected by the difference in the incubation time of the deposition (Fig. 4). No incubation time was found in the deposition using DER.

The bright contrast layers were observed at the Ru/TaN interface region. It was confirmed that these layers had the lower density than that of Ru and TaN layers by XRR analysis. It is assumed that these low density layers are formed by nitridation of PVD-TaN under NH<sub>3</sub> plasma irradiation. In order to confirm that the low density layer is formed by the nitridation,

The dependences of Ru film thickness per 300 deposition cycles and of the film density on the NH<sub>3</sub> pulse time (NH<sub>3</sub> plasma ignition time) are shown in Fig. 5. The thicknesses per deposition cycles were constant for DER. For Ru(EtCp)<sub>2</sub>, the thickness per deposition cycles slightly increased with NH<sub>3</sub> pulse time. It is supposed that thickness per deposition cycles for DER immediately saturated against NH<sub>3</sub> pulse because of their easy decomposition nature. The dependences on the RF

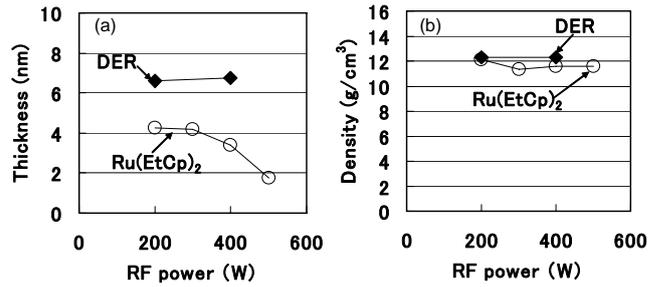


Fig. 6. RF power dependence of (a) Thickness, (b) Density.

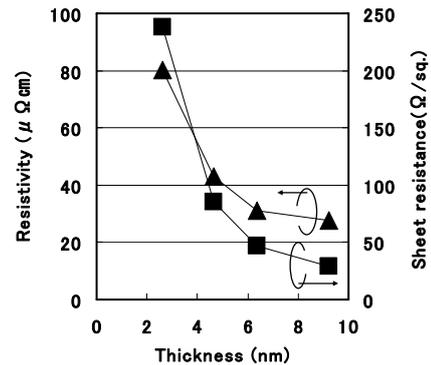


Fig. 7. The resistivities of various thicknesses Ru films deposited using DER precursor.

power of NH<sub>3</sub> plasma are also shown in Fig. 6. The thickness per deposition cycle for DER was saturated over RF power of 200 W. Therefore, RF power of 200W is adequate for PE-ALD using DER precursor. The resistivities and sheet resistances of various thicknesses Ru films deposited using DER precursor are shown in Fig. 7. The resistivities in the range of less than 100 μΩ cm for thickness of 3 – 9 nm are acceptable for the direct Cu ECD.

## Conclusion

Using DER as Ru precursor, the incubation time of Ru films deposition was improved to almost zero, and the surface morphology of Ru film became smooth at the stage temperature of 300 C. These results are assumed that DER is easily decomposed at low temperature under NH<sub>3</sub> plasma. The resistivity of PE-ALD Ru films were in the range of less than 100 μΩ cm. Thus, it is concluded that DER is one of the suitable precursors for PE-ALD on TaN.

## Acknowledgment

The authors would like to thank to S. Saito and N. Kobayashi for their fruitful discussion.

## References

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