●A Novel MO Precursor for Tantalum Containing Film

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1. Introduction

Tantalum nitride (TaN) is used for a diffusion barrier film in copper (Cu) interconnects. Since TaN has poor adhesion to Cu, an adhesive layer is put between TaN and Cu film. A metal tantalum (Ta) film is one of the candidates for the adhesive layer. In the current process, the Ta/TaN laminated film is deposited by physical vapor deposition (PVD). Whereas the barrier film is required to be thinner and more conformal with shrinkage of the interconnect dimensions. Thus, chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes have been investigated as a new deposition method.

Several tantalum compounds have been investigated for the precursors of CVD and ALD processes. Tantalum amide complexes such as pentakis (dimethylamido)tantalum (PDMAT) [1] and tert-butylimido tris(diethylamido)tantalum (TBTDET) [2,3] contain nitrogen atoms in the molecules. Therefore, it is difficult to make a metal tantalum film. Halogen atoms in tantalum halides ($TaCl_5$ and $TaBr_5$) [4] are cause of corrosion or poor adhesion.

We developed the novel tantalum compound, bis(ethylcyclopentadienyl)hydridocarbonyltantalum ($Ta(EtCp)_2(CO)H$, **Fig. 1**), for CVD and ALD process which have neither nitrogen nor halogen atom. In this paper, we introduce physical properties and film deposition results of this precursor.

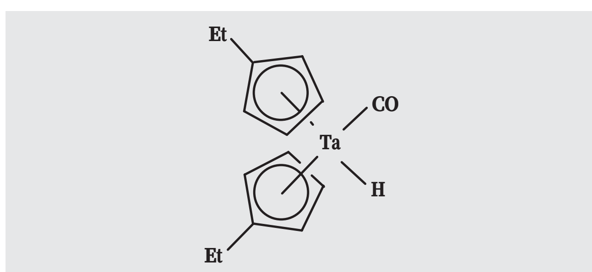

Fig. 1 Molecular structure of $Ta(EtCp)_2(CO)H$

2. Synthesis of precursor

$Ta(EtCp)_2(CO)H$ was synthesized from bis (ethylcyclopentadienyl)trihydridotantalum ($Ta(EtCp)_2H_3$) and CO. The former trihydride complex was prepared following the literature method [5]. $Ta(EtCp)_2(CO)H$ was purified by distillation under a reduced pressure. This precursor was purple liquid at room temperature (mp = 15 ℃). The molecular structure was confirmed by nuclear magnetic resonance spectroscopy (NMR), infra red spectroscopy (IR), inductively coupled plasma - atomic emission spectrometry (ICP-AES) and elemental analysis. The structure estimated by ^{1}H-NMR reasonably explained the ^{13}C-NMR spectrum. These spectroscopic data and the result of the elemental analysis conclude the molecular structure in **Fig. 1.**

^{1}H-NMR (Benzene-d_6, δ ppm)

4.53(m, 2H, $C_5\underline{H}_4Et$), 4.46(m, 2H, $C_5\underline{H}_4Et$), 4.42(m, 2H, $C_5\underline{H}_4Et$), 4.35(m, 2H, $C_5\underline{H}_4Et$), 2.26(m, 4H, $CH_3C\underline{H}_2C_5H_4$), 1.00(t, J=7.5Hz, 6H, $C\underline{H}_3CH_2C_5H_4$), -6.16(s, 1H, Ta-$\underline{H}$)

^{13}C-NMR (Benzene-d6, δ ppm)

264.26($\underline{C}O$), 112.38($\underline{C}_5H_4Et$), 83.71($\underline{C}_5H_4Et$), 83.40($\underline{C}_5H_4Et$), 82.08($\underline{C}_5H_4Et$), 79.61($\underline{C}_5H_4Et$), 23.26($CH_3\underline{C}H_2C_5H_4$), 15.92($\underline{C}H_3CH_2C_5H_4$)

IR(Nujol, ν cm^{-1})

1896(CO), 1721(Ta-H)

Elemental analysis and ACP-AES

Found (calculated) C: 46.2%(45.5%) H: 5.1%(4.8%) Ta: 46.4%(45.7%)

(Tantalum content was measured by ICP-AES.)

3. Physical properties of precursor

[1] Vaporizing and decomposition characteristics

The vaporizing and decomposition characteristics were investigated with thermo gravimetric (TG) and differential scanning calorimetric (DSC) curves

obtained under an argon atmosphere.

Fig. 2 illustrates the TG and DSC curves of $Ta(EtCp)_2(CO)H$, and revealed that the vaporizing and decomposition temperature of the precursor is 130 ℃ (TG) and 240 ℃ (DSC), respectively. Thus, the precursor vaporizes without any decomposition.

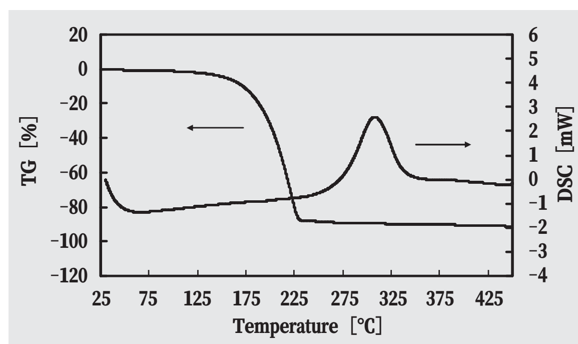

Fig. 2 The TG and DSC curves of $Ta(EtCp)_2(CO)H$ under an argon atmosphere at a heating rate of 10℃/min.

[2] Vapor pressure

The vapor pressure was determined by a static method. **Fig. 3** depicts the vapor pressures of $Ta(EtCp)_2(CO)H$ at various temperatures. The formula of vapor pressure = $1.68 \times 10^{11} \times \exp(-8.87 \times 1000/T)$ was obtained from the curve of 1000/T vs. vapor pressure. The vapor pressure calculated from this formula is 1 Pa at 70 ℃ and 8 Pa at 100 ℃. These values suggest that this precursor is volatile enough to be used in the CVD and ALD process.

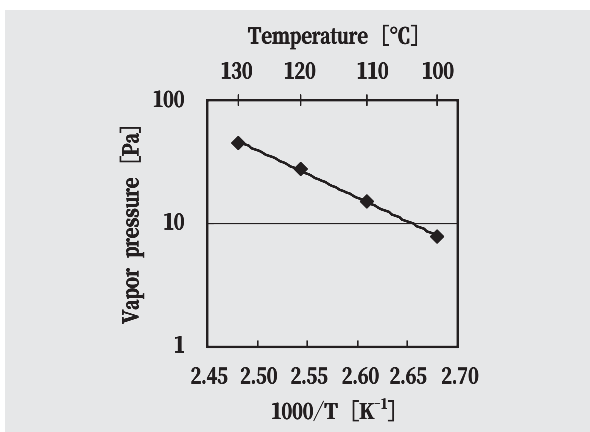

Fig. 3 Vapor pressure diagram of $Ta(EtCp)_2(CO)H$

[3] Thermal stability

Thermal stability was confirmed by changes of ^{1}H-NMR before and after heating. This precursor had no changes after 24 hours at 170 ℃ and 96 hours at 140 ℃.

[4] Viscosity

The viscosity was measured by B type Viscometer. **Fig. 4** shows the viscosity diagram of $Ta(EtCp)_2(CO)H$. This diagram indicates that this precursor can be used in direct liquid injection by heating. In addition, this precursor dissolves in hydrocarbon solvents. So it also can be used in liquid injection as solution.

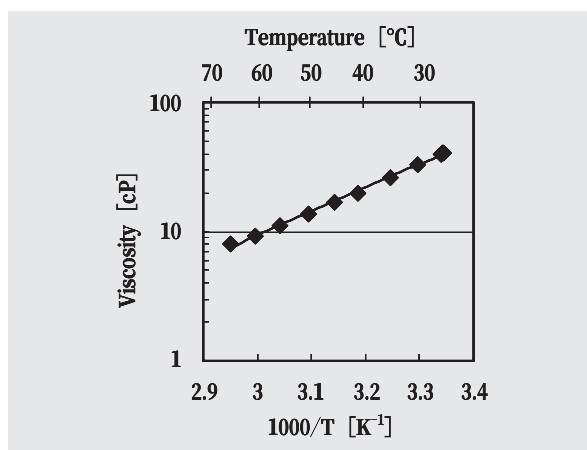

Fig. 4 Viscosity diagram of $Ta(EtCp)_2(CO)H$

4. Film deposition

Film depositions on Si/SiO_2 or Si substrates were performed using cold wall type thermal CVD and electron cyclotron resonance (ECR) plasma CVD equipments. The vapor of the precursor was generated by bubbling method. The film thicknesses were determined from TEM images. The resistivities of the films were measured using a standard four-probe method. The compositions of the films were analyzed by auger electron spectroscopy (AES).

[1] Film deposition by thermal CVD

The metal tantalum film deposition was attempted by the thermal CVD. The deposition condition is summarized in **Table 1**.

The resistivity of the film deposited below 500 ℃ was too high to measure it with the standard method. The resistivity of the film deposited at 600 ℃ could be determined to be 1.78×10^5 μΩcm (film thickness was 250nm); it is still high for the adhesive layer of Cu interconnects. The high resistivity will be due to the contamination of carbon. Actually, the AES depth

Tabel 1　Experimental condition by thermal CVD

Bubbler Temperature	90°C	Deposition Pressure	1.33kPa
Bubbler Pressure	13.3kPa	Deposition Time	120min
Carrier gas (Ar) flow rate	100sccm	Substrate	Si/SiO_2
Dilute gas (Ar) flow rate	100sccm	Substrate Temperature	600°C
Total flow rate	200sccm		

profiles of deposited film at 600 °C revealed 55atom% carbon and 10atom% oxygen in the film as shown in **Fig. 5**. The high carbon concentration may be derived from incomplete thermal decomposition of the precursor.

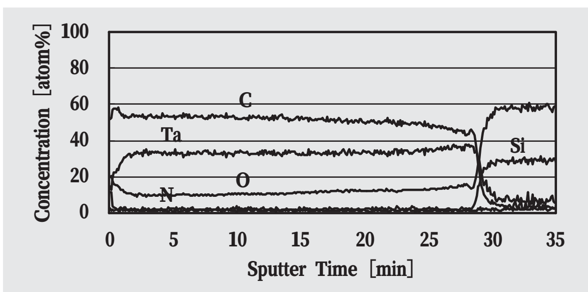

Fig. 5　The composition of film deposited by thermal CVD.

[2] Film deposition by ECR plasma CVD

In order to decompose the precursor completely, the ECR plasma CVD technique was investigated. The deposition condition is summarized in **Table 2**.

The film thickness of the obtained film was 7.2nm and its resistivity was 143 μΩcm. **Fig. 6** shows the AES depth profiles of the deposited film. The carbon concentration decreased to about 50% of that in the film deposited by thermal CVD, indicating that the ECR plasma CVD decomposes the precursor more than the thermal CVD.

[3] Film deposition by ECR plasma CVD with 4% hydrogen gas

Furthermore, ECR plasma CVD deposition in the

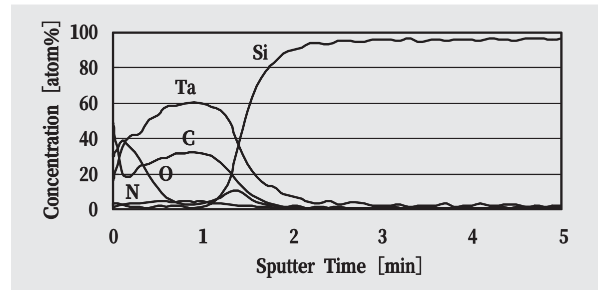

Fig. 6　The composition of film deposited by ECR plasma CVD.

presence of hydrogen gas was examined in order to reduce the carbon concentration in the film. The deposition condition is summarized in **Table 3**.

Argon gas, which added 4% of hydrogen gas, was used as a source of plasma. The film thickness of the obtained film was 14.3nm. **Fig. 7** shows the AES depth profile of the film. Although carbon concentration increased slightly, the resistivity decreased to 109 μΩcm. This result is assumed to be due to decrease of oxygen concentration in the film.

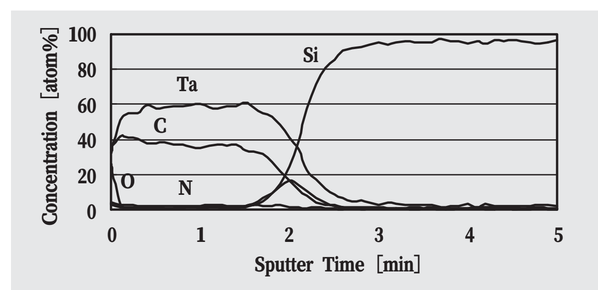

Fig. 7　The composition of film deposited by ECR plasma CVD with 4% hydrogen gas

Tabel 2　Experimental condition by ECR plasma CVD

Bubbler Temperature	90°C	Deposition Pressure	0.2kPa
Bubbler Pressure	6.67kPa	Deposition Time	30min
Carrier gas (Ar) flow rate	28sccm	Substrate	Si
Plasma Source gas (Ar) flow rate	10sccm	Substrate Temperature	400°C
Total flow rate	38sccm	Plasma Power	600W

Tabel 3 Experimental condition by ECR plasma CVD with 4% hydrogen gas

Bubbler Temperature	90℃	Deposition Pressure	1.0kPa
Bubbler Pressure	9.33kPa	Deposition Time	300min
Carrier gas (Ar) flow rate	55sccm	Substrate	Si
Plasma Source gas (Ar/H_2) flow rate	40sccm (H_2:1.6sccm)	Substrate Temperature	300℃
Total flow rate	95sccm	Plasma Power	600W

5. Conclusions

A novel tantalum precursor for CVD and ALD, $Ta(EtCp)_2(CO)H$, which is nitrogen and halogen free and liquid phase at room temperature, was developed. The vapor pressure and decomposition temperature indicates that this precursor is suitable for CVD and ALD process.

The film deposited by the thermal CVD at 600 ℃ contained the large amount of carbon and have high resitivity. On the other hand, the carbon concentration in the film deposited by the ECR plasma CVD at 400 ℃ was about half of that in the film deposited by the thermal CVD, resulting in the low resistivity. Furthermore the film deposited by the ECR plasma CVD in the presence of 4% hydrogen gas had lower resistivity.

6. References

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