Low temperature MOCVD of Ta₂O₅ dielectric thin films from Ta[NC(CH₃)₃][OC(CH₃)₃]₃ and O₂

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Ta₂O₅ thin films were deposited at 155–400°C on amorphous SiO₂ and Pt/TiO_x/SiO₂/Si substrates by metal organic chemical vapor deposition (MOCVD) from tri(*tert*-butoxy)(isopropylimido)tantalum [Ta[NCH(CH₃)₂][OC(CH₃)₃]₃]-O₂, tri(*tert*-butoxy)-(*tert*-butylimido)tantalum [Ta[NC(CH₃)₃][OC(CH₃)₃]₃]-O₂ and pentaethoxy tantalum [Ta(OC₂H₅)₅]-O₂ systems. Temperature dependency of the deposition rate was almost the same for the films from Ta[NCH(CH₃)₂][OC(CH₃)₃]₃-O₂ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ systems irrespective of the kinds of substrates, and the deposition rate of these two systems was higher than that of Ta(OC₂H₅)₅-O₂ system for all deposition temperature range within the present study. Dielectric properties of Ta₂O₅ thin films deposited on Pt/TiO_x/SiO₂/Si substrates at 200°C from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system and at 300°C from Ta(OC₂H₅)₅-O₂ system were also investigated. In spite of their 100°C lower deposition temperature, the Ta₂O₅ films from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system showed lower leakage current density and almost the same dielectric constant with those from Ta(OC₂H₅)₅-O₂ system.

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1. Introduction

Thin films of tantalum pentoxide (Ta₂O₅) have been extensively investigated as a dielectric layer candidate of capacitors for dynamic random access memories (DRAMs) due to its relative high dielectric constant and low leakage characteristics.^{1)–3)} A number of techniques have been used to deposit Ta₂O₅ films.^{4)–6)} However, metal organic chemical vapor deposition (MOCVD) and its modified atomic layer deposition (ALD) have an advantage to deposit thin films on a three-dimensional surface with a uniform thickness and good conformability that enable the high capacitor densities on the same foot print area.^{7)–9)} Although tantalum chloride (TaCl₅)^{10)–13)} and pentaethoxy tantalum [Ta(OC₂H₅)₅]^{14)–16)} have been widely studied as MOCVD and ALD precursors to deposit Ta₂O₅ films, more volatile precursors which realize high deposition rate are required for semiconductor manufacturing for the scaling up of the substrates size by the increase of the supply rate of the Ta sources and high productivity. For this reason, we reported the synthesis method, physical properties, and deposition characteristics of a novel highly volatile precursor for Ta₂O₅ thin films, tri(*tert*-butoxy)(*tert*-butylimido)tantalum [Ta[NC(CH₃)₃][OC(CH₃)₃]₃] in the previous paper¹⁷⁾ because it was predicted that the imido ligand (=N–R) in Ta[NC(CH₃)₃][OC(CH₃)₃]₃ is more reactive towards oxygen than

alkoxy group (–OR). As a result, the deposition rate of Ta₂O₅ films from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system was ascertained to be higher than that from conventional tantalum alkoxide precursor, Ta(OC₂H₅)₅-O₂ system.

In this paper, we investigated an additional Ta source, tri(*tert*-butoxy)(isopropylimido)tantalum [Ta[NCH(CH₃)₂][OC(CH₃)₃]₃], to identify the origin of the deposition behavior difference between Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ and Ta(OC₂H₅)₅-O₂ systems. Deposition characteristics were also investigated for the films deposited on amorphous SiO₂ and platinized Si substrates. In addition, dielectric and leakage current characteristics were compared for these films.

2. Experimental procedure

2.1 Precursors

Figure 1 shows the molecular structures of Ta sources investigated in the present study. Ta(OC₂H₅)₅ is illustrated as a dimer.¹⁸⁾ The synthesis, thermal and physical properties of Ta[NC(CH₃)₃][OC(CH₃)₃]₃ were reported in our previous reports.¹⁷⁾ Ta(OC₂H₅)₅ was supplied from Aldrich Co. On the other hand, Ta[NCH(CH₃)₂][OC(CH₃)₃]₃ was prepared by the following method; a lithium *tert*-butoxide solution, which was prepared from 1.49 g of *tert*-butyl alcohol and 12.7 mL of butyl lithium/hexane solution (1.58 M), was added into the solution of trichloro(isopropylimido)bis(pyridine)tantalum¹⁹⁾ (3.36 g, 6.68 mmol) in 15 mL toluene. The resulting mixture was stirred at ambient temperature for 12 h. After the insoluble substance was filtered out, the filtrate was distilled under reduced pressure to give 2.65 g of Ta[NCH(CH₃)₂][OC(CH₃)₃]₃ as colorless oil, 87% yield.

¹H NMR (500 MHz, C₆D₆, δ): 4.31 [sept, *J* = 7 Hz, 1 H,

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Fig. 1. Molecular structures of $\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3$, $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3$, and $[\text{Ta}(\text{OC}_2\text{H}_5)_5]_2$.Table 1. Physical properties of $\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3$, $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3$, and $\text{Ta}(\text{OC}_2\text{H}_5)_5$

Precursor	$\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3$	$\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3$	$\text{Ta}(\text{OC}_2\text{H}_5)_5$
Molecular weight	457.4	471.4	812.5
Temperature at the vapor pressure of 0.1 Torr °C	47	46	129
Phase at room temperature	liquid	liquid	liquid
Complexity	1	1	2

$\text{NCH}(\text{CH}_3)_2$], 1.38 [s, 27H, $\text{OC}(\text{CH}_3)_3$], 1.31 [d, $J = 7$ Hz, 6H, $\text{NCH}(\text{CH}_3)_2$]. ^{13}C NMR (125 MHz, C_6D_6 , δ): 78.1 [$\text{OC}(\text{CH}_3)_3$], 61.0 [$\text{NCH}(\text{CH}_3)_2$], 32.9 [$\text{OC}(\text{CH}_3)_3$], 28.9 [$\text{NCH}(\text{CH}_3)_2$].

Vapor pressures of the precursors were estimated with a diaphragm gauge (BaratronTM) placed in a thermostatic oven.

The complexity of $\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3$ and $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3$ was estimated by measurement of weight loss of the precursor after vaporizing a certain volume of precursor gas. Literature data was used for $\text{Ta}(\text{OC}_2\text{H}_5)_5$.¹⁸⁾

2.2 MOCVD of Ta_2O_5 film

Ta_2O_5 films were deposited on amorphous SiO_2 and platinized Si (Pt/ TiO_x / SiO_2 /Si) substrates using a cold-wall-type thermal MOCVD apparatus.¹⁷⁾ The vapors of the precursors were obtained by bubbling 30 cm^3/min of argon gas through them, and were introduced into the reaction chamber with 60 cm^3/min of oxygen gas as a reactant. Vapor pressure of the precursor was set to be 0.55 Torr for $\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3$ and $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3$, and 0.29 Torr for $\text{Ta}(\text{OC}_2\text{H}_5)_5$ by adjusting the temperature of the precursors. The deposition pressure was set to be 4 Torr.

2.3 Characterization

The deposition rates of Ta_2O_5 films were calculated from the film thickness divided by the deposition time. The film thickness was estimated by a field emission scanning electron microscope (FE-SEM) using JSM-7600F (JEOL Ltd.) and X-ray fluorescence analysis (XRF) using 3370E (Rigaku Corporation). Atomic force microscope (AFM) using Nano Scope IIIa (Bruker AXS Co., Ltd.) was performed to observe the surface morphology.

In order to make metal-insulator-metal (MIM) capacitor structure for the electrical property characterization, Ta_2O_5 films were deposited on Pt/ TiO_x / SiO_2 /Si substrates, and Pt top electrodes were deposited on Ta_2O_5 films through the metal shadow mask by electron beam evaporation. Deposited Pt top electrodes were circle patterns with the area of about $9.9 \times 10^{-3} \text{ mm}^2$. The capacitance–voltage (C–V) characteristic was measured at room temperature and a frequency of 100 kHz with HP4194A impedance analyzer (Agilent Technologies). Current density–voltage (J–V) characteristic was analyzed at room temperature

Fig. 2. Temperature dependency of the deposition rate for Ta_2O_5 films deposited for 60 min on amorphous SiO_2 substrates from $\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3\text{-O}_2$, $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3\text{-O}_2$, and $\text{Ta}(\text{OC}_2\text{H}_5)_5\text{-O}_2$ systems.

with HP4155B semiconductor parameter analyzer (Agilent Technologies).

3. Results and discussion

3.1 Physical property of precursors

Physical properties of these three precursors are summarized in Table 1. These three precursors are all liquid state at room temperature. Vapor pressures of $\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3$ and $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3$ were almost the same and were higher than that of $\text{Ta}(\text{OC}_2\text{H}_5)_5$. This is because $\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3$ and $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3$ exist as a monomer, while $\text{Ta}(\text{OC}_2\text{H}_5)_5$ exists as a dimer. It must be noted that $\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3$ and $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3$ showed almost the same physical properties due to the similarity of the structures and small difference of the molecular weights.

3.2 Deposition behavior of Ta_2O_5 films

Figure 2 shows a relationship between the deposition temperature and the deposition rate for the Ta_2O_5 films deposited for 60 min on amorphous SiO_2 substrates from $\text{Ta}[\text{NCH}(\text{CH}_3)_2][\text{OC}(\text{CH}_3)_3]_3\text{-O}_2$, $\text{Ta}[\text{NC}(\text{CH}_3)_3][\text{OC}(\text{CH}_3)_3]_3\text{-O}_2$ and $\text{Ta}(\text{OC}_2\text{H}_5)_5\text{-O}_2$

Fig. 3. Cross-sectional FE-SEM images of Ta₂O₅ thin films deposited on amorphous SiO₂ hole with an aspect ratio of 6 from (a) Ta[NCH(CH₃)₂][OC(CH₃)₃]₃-O₂ system at 200°C, (b) Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system at 200°C, and (c) Ta(OC₂H₅)₅-O₂ system at 300°C.

Fig. 4. Temperature dependency of the deposition rate for Ta₂O₅ films deposited for 60 min on amorphous SiO₂ and Pt/TiO_x/SiO₂/Si substrates from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system and Ta(OC₂H₅)₅-O₂ system.

O₂ systems. Deposition rates of Ta₂O₅ films were almost the same for Ta[NCH(CH₃)₂][OC(CH₃)₃]₃-O₂ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ systems; the deposition rate of Ta₂O₅ films was less sensitive against the deposition temperature above 250°C, while strong deposition temperature dependency was observed below 200°C. This critical deposition temperature for deposition rate was shifted to be higher temperature between 325 and 400°C for Ta(OC₂H₅)₅-O₂ system.

Noticeable thing is that the deposition rate of Ta₂O₅ films from Ta[NCH(CH₃)₂][OC(CH₃)₃]₃-O₂ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ systems was higher than that from Ta(OC₂H₅)₅-O₂ system for all temperature range investigated in the present study. Another remarkable point is that the deposition of Ta₂O₅ films was detected above 155°C from Ta[NCH(CH₃)₂][OC(CH₃)₃]₃-O₂ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ systems and this temperature was lower than that from Ta(OC₂H₅)₅-O₂ system, above 200°C.

Figure 3 shows cross-sectional FE-SEM images of Ta₂O₅ thin films deposited on amorphous SiO₂ hole with an aspect ratio of 6 from (a) Ta[NCH(CH₃)₂][OC(CH₃)₃]₃-O₂ system at 200°C, (b) Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system at 200°C, and (c) Ta(OC₂H₅)₅-O₂ system at 300°C. The film thickness changes from the top to the bottom of the side wall were found to be over 90% for all films. All these precursors show pretty good step coverage without overhang at the upper corner.

Figure 4 displays a relationship between the deposition rate

Fig. 5. AFM topographic images of Ta₂O₅ films deposited at 200°C on (a) amorphous SiO₂ and (b) Pt/TiO_x/SiO₂/Si substrates from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system.

and the deposition temperature for the Ta₂O₅ films deposited for 60 min at various temperatures on amorphous SiO₂ and Pt/TiO_x/SiO₂/Si substrates from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ and Ta(OC₂H₅)₅-O₂ systems. Noticeable change with the kinds of substrates was not detected between amorphous SiO₂ and Pt/TiO_x/SiO₂/Si substrates for both source systems. This result clearly showed the kinds of Ta source more strongly influenced on the deposition characteristics than the kinds of substrates.

Similar deposition rate from Ta[NCH(CH₃)₂][OC(CH₃)₃]₃-O₂ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ systems observed in Fig. 2 indicates that the alkyl group of imido ligand (=N-R) in Ta[NCH(CH₃)₂][OC(CH₃)₃]₃ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃ have little influence on the deposition rate. In contrast, the introduction of imido ligand (=N-R) into alkoxide complex as Ta[NCH(CH₃)₂][OC(CH₃)₃]₃ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃ have a great influence on the physical properties and deposition rates of Ta₂O₅ films as compared to that of alkoxide complex, Ta(OC₂H₅)₅. Another difference between Ta[NCH(CH₃)₂][OC(CH₃)₃]₃ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃, and Ta(OC₂H₅)₅ is the complexity. Ta[NCH(CH₃)₂][OC(CH₃)₃]₃ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃ are a monomer while Ta(OC₂H₅)₅ is a dimer, and this difference may change their reactivity with reactant gas. For example, pentaisopropoxy tantalum [Ta(OC₃H₇)₅] is a monomeric alkoxide complex due to its bulky alkoxy group.⁵⁾ The vapor pressure of Ta(OC₃H₇)₅ is 0.1 Torr at 87°C and higher than that of dimeric Ta(OC₂H₅)₅. However, the melting point of Ta(OC₃H₇)₅ is 107°C and it is solid at room temperature. This example shows that monomeric alkoxide complexes with bulky alkoxy group have possibility to influence CVD process because these complexes need high temperature for precursor gas delivery system. These results indicate that the introduction of imido ligand (=N-R) into alkoxide complex improved physical and deposition properties of the precursors simultaneously to deposit Ta₂O₅ films.

3.3 Characterization of deposited films

To evaluate electrical properties, Ta₂O₅ thin films deposited on amorphous SiO₂ and Pt/TiO_x/SiO₂/Si substrates from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ and Ta(OC₂H₅)₅-O₂ systems were investigated.

Figure 5 shows the AFM topographic images of 40–50 nm-thick Ta₂O₅ films deposited at 200°C on amorphous SiO₂ and Pt/TiO_x/SiO₂/Si substrates from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system. The average surface roughness (*Ra*) was 0.11 and 0.14 nm for the films deposited on amorphous SiO₂ and Pt/TiO_x/SiO₂/Si substrates, respectively.

Fig. 6. Relative dielectric constant and dielectric dissipation factor ($\tan \delta$) vs. applied voltage for Pt/Ta₂O₅/Pt MIM capacitors for Ta₂O₅ films deposited from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system at 200°C and from Ta(OC₂H₅)₅-O₂ system at 300°C, respectively.

Fig. 7. Current density vs. applied voltage for Pt/Ta₂O₅/Pt MIM capacitors for the same Pt/Ta₂O₅/Pt MIM capacitors shown in Fig. 6.

Dielectric constant of the as-deposited films was characterized by C-V measurement as shown in Fig. 6 using Pt/Ta₂O₅/Pt capacitor structure for 53 and 42 nm-thick Ta₂O₅ films deposited at 200 and 300°C from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ and Ta(OC₂H₅)₅-O₂ systems, respectively. At positive voltage region, the voltage was applied from top Pt electrode to the bottom Pt electrode, and applied reverse direction at negative voltage region. The dielectric constant was almost independent of the applied voltage up to ± 3 V and was 26 and 27 for films from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ and Ta(OC₂H₅)₅-O₂ systems, respectively. These values are almost the same and are almost consistent with the reported value of about 25 by many groups in the literature.^{1)-5),8)} In addition, the dielectric dissipation factor ($\tan \delta$) of these films was also close.

Figure 7 compares the leakage current density vs. applied voltage (J-V) for the same Pt/Ta₂O₅/Pt MIM capacitors shown in Fig. 6. There was no significant difference in leakage current density between these two films at the voltage region from 0 to 3 V, however, the leakage current density of the films from Ta(OC₂H₅)₅-O₂ system increased significantly at negative voltage region compared to that from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system. The difference between positive and negative voltage regions is considered to be occurred by the difference of the thermal treatment between the top and bottom interfaces between

Ta₂O₅ films and Pt electrodes; interface between Ta₂O₅ film and bottom Pt electrode was heat-treated at the deposition temperature during Ta₂O₅ film deposition that was possible to induce the interdiffusion, while this heat treatment effect is considered to be small for the interface between Pt top electrode and Ta₂O₅ film during Pt top electrode deposition at room temperature. Based on these consideration, the difference of the leakage current data at negative voltage region between the films from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system and those from Ta(OC₂H₅)₅-O₂ system is supposed to be mainly originated with the difference of the deposition temperature. Compared to the films from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system, the deposition temperature was 100°C higher for the films from Ta(OC₂H₅)₅-O₂ system that might change the interface between Ta₂O₅ and Pt bottom electrodes and change the leakage current density. Overall, as-deposited Ta₂O₅ films from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system showed lower leakage current density, almost equivalent dielectric constant, and comparable dielectric dissipation factor than that from Ta(OC₂H₅)₅-O₂ system in spite of their 100°C lower deposition temperature.

These results show that Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system is a novel candidate to get the Ta₂O₅ films by MOCVD at lower temperature with good dielectric and insulating characteristics.

4. Conclusions

The deposition characteristics of Ta₂O₅ films from Ta[NCH(CH₃)₂][OC(CH₃)₃]₃-O₂, Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ and Ta(OC₂H₅)₅-O₂ systems were investigated. Deposition behavior of Ta₂O₅ films were almost the same with that from Ta[NCH(CH₃)₂][OC(CH₃)₃]₃-O₂ and Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ systems, but was different from Ta(OC₂H₅)₅-O₂ system. Large influence of imido ligand introduction for alkoxide complex was suggested. Electrical properties of Ta₂O₅ thin films deposited at 200°C from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system and those at 300°C from Ta(OC₂H₅)₅-O₂ system were also investigated by Pt/Ta₂O₅/Pt structure for the Ta₂O₅ films deposited on Pt/TiO_x/SiO₂/Si substrates. The Ta₂O₅ films from Ta[NC(CH₃)₃][OC(CH₃)₃]₃-O₂ system showed lower leakage current density and almost the same dielectric constant with that from Ta(OC₂H₅)₅-O₂ system in spite of their 100°C lower deposition temperature.

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