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Atomic layer deposition of ZrO_2 thin film on Si(100) using $\{\eta^5:\eta^1\text{-Cp}(CH_2)_3NMe\}Zr(NMe_2)_2/O_3$ as precursors

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ABSTRACT

Atomic layer deposition (ALD) of ZrO_2 thin films was investigated using a linked cyclopentadienyl-amido compound of zirconium, $\{\eta^5:\eta^1\text{-Cp}(CH_2)_3NMe\}Zr(NMe_2)_2$ with ozone. The ALD-window was established as 300–380 °C with a growth rate of about 0.95 Å/cycle. A good film conformality of 0.95 for 5.7–6.1 nm-thick film was obtained for bottom and sidewall step coverages of 0.93 and 0.95, respectively. The ALD at 330 °C yielded a ZrO_2 having good crystallinity. The film showed low impurity levels and a strong tendency to form the tetragonal/cubic phases despite a low film thickness of 8.58 nm (root-mean-square roughness = 0.49 nm). Better ALD performance was obtained with this linked precursor than with the commonly used $CpZr(NMe_2)_3$ precursor. Furthermore, theoretical calculations for the ALD processes on hydroxylated Si wafer surfaces were performed by using density function theory. Initial growth mechanism of ZrO_2 from $CpZr(NMe_2)_3$ and $\{\eta^5:\eta^1\text{-Cp}(CH_2)_3NMe\}Zr(NMe_2)_2$ were proposed on atomic-scale structure.

1. Introduction

High-*k* dielectric materials have attracted great attention because of their broad applications in modern microelectronics. These applications include gate oxides in metal-oxide-semiconductor (MOS) devices and insulators in metal–insulator–metal capacitors [1–3]. Downscaling of the structural features in MOS devices has reached the limit of the traditional SiO_2 layer in the application to the nanosized configurations, which require extremely low leakage current. Leakage current density must be $<10^{-7}$ A/cm^2 at gate voltage of 1–3 V for the dynamic random access memory. Thin-layer SiO_2 with a thickness of 1.5 nm has a high gate-leakage current of 10 A/cm^2 at 1 V, which arises from its high electron tunneling current. Thus, it is necessary to replace the SiO_2 ($k = 3.9$) by high-*k* metal oxides [4]. ZrO_2 has been extensively investigated as alternative materials for SiO_2 [5–8] because of its high κ value with 37–47 [9] and thermal stability on Si substrate [10]. Atomic layer deposition (ALD) technology has proven to be an excellent method to deposit high-quality ultrathin films with uniform thicknesses and smooth surfaces [11]. Cyclopentadienyl-type (Cp-type) Zr compounds, such as $(RCp)Zr(NMe_2)_3$ (R = H, Me or Et) [12,13], $(MeCp)_2ZrMe_2$ or $(MeCp)_2ZrMe(OMe)$ [14–19], Cp_2ZrMe_2 [20] and (RCp)Zr(CHT) (CHT = cycloheptatrienyl) [21,22] have attracted great interest as ALD precursors for ZrO_2 ultrathin film deposition. The Cp ligand in Zr compounds enhances thermal stability and allows the deposition temperature of above 300 °C, and provides thin films having good crystallinity. Among those precursors, the $(RCp)Zr(NMe_2)_3$ ones resulted in films having the best conformity (0.82) and the highest growth rate (0.9 Å/cycle at 300 °C). Currently, RCp-ligands in Zr precursors provided some advantages in depositing ultrathin films of ZrO_2 on an Si(100) substrate. However, some precursors are required to fabricate better-quality ZrO_2 films on Si.

In this paper, we introduced $\{\eta^5:\eta^1\text{-Cp}(CH_2)_3NMe\}Zr(NMe_2)_2$ as a precursor and analyzed the ALD growth characteristics to obtain the best possible film properties. Chart 1 shows that the cyclopentadienyl-N-methylpropane-1-amindo ligand forms a linked configuration with Zr(IV). In this study, $CpZr(NMe_2)_3$ was also used for the fabrication of ZrO_2 thin films. Comparison of the two Zr precursors revealed that the linked $\{\eta^5:\eta^1\text{-Cp}(CH_2)_3NMe\}Zr(NMe_2)_2$ was a highly efficient precursor for the ALD of ZrO_2 and allowed the growth of high-quality films with excellent properties. Furthermore, the geometric optimization was performed for the precursor chemisorbed on Si(100) surface. The results provided useful information about initial decomposition properties for the ALD process.

2. Experimental details

2.1. Analysis of the precursors

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 spectrometer at room temperature in C_6D_6 solution (using residual C_6H_6 as internal reference for ^1H NMR). Thermogravimetric

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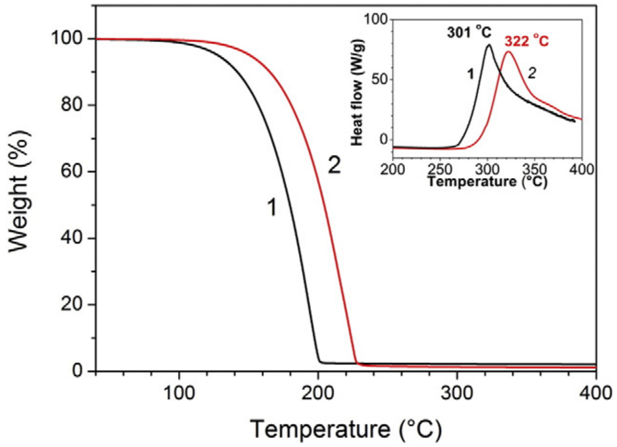

Fig. 1. TGA curves for $CpZr(NMe_2)_3$ (1) and $\{\eta^5{:}\eta^1\text{-}Cp(CH_2)_3NMe\}Zr(NMe_2)_2$ (2) (the insertion: DSC curves).

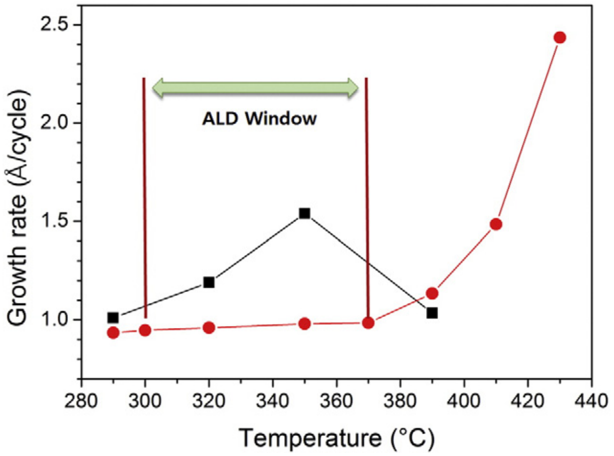

Fig. 3. Growth rate of ZrO_2 thin films as a function of temperature when deposited from $CpZr(NMe_2)_3$ (square) and $\{\eta^5{:}\eta^1\text{-}Cp(CH_2)_3NMe\}Zr(NMe_2)_2$ (circle) with ozone.

analysis (TGA) was carried out on a TA Instruments Model Q600 instrument in a glovebox (H_2O 0.1 ppm, O_2 1 ppm). Ar (99.9999%) flow was applied at 200 sccm to an aluminium crucible containing 20 mg of the precursor. Thermal decomposition temperatures of the prepared precursors were investigated using a TA Instruments Model Q-10 differential scanning calorimeter (DSC).

2.2. Syntheses

2.2.1. Synthesis of $Zr(NMe_2)_4$ and $CpZr(NMe_2)_3$

All manipulations were performed under dry Ar gas using standard Schlenk techniques. A 10 L three-neck flask was charged with 3.3 L of toluene, 2.5 M of n-BuLi (1.68 L, 4.21 mol) dissolved in hexane was added and then cooled to −15 to −20 °C. $HNMe_2$ (245 g, 5.46 mol) was slowly added, and then the reaction mixture was warmed to 60 °C and then stirred for 5 h. After removing the excess of $HNMe_2$, the reaction mixture was cooled to room temperature and powdered $ZrCl_4$ (1.0 mol) was slowly added to the stirred solution. The reaction mixture was refluxed at 80 °C for 4 h to form the crude $Zr(NMe_2)_4$. After cooling to −10 to −15 °C, cyclopentadiene monomer (79.2 g, 1.2 mol) was added to the stirring mixture. The solids were removed by filtration and all volatile species were removed by evaporation. The pure product, $CpZr(NMe_2)_3$, a clear yellow liquid (202 g, 0.61 mol, 61%), was obtained by fractional vacuum distillation. ^1H NMR (C_6D_6): δ 6.06 (s, 4H), 2.92 (s, 18H).

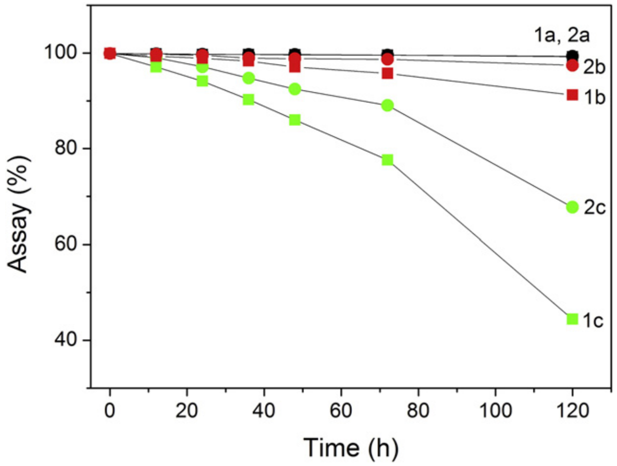

Fig. 2. Decomposition rates of $CpZr(NMe_2)_3$ (square, 1) and $\{\eta^5{:}\eta^1\text{-}Cp(CH_2)_3NMe\}Zr(NMe_2)_2$ (circle, 2) at 140 °C (a), 160 °C (b) and 180 °C (c) under vacuum.

2.2.2. Synthesis of $Cp(CH_2)_3NHMe$ and $\{\eta^5{:}\eta^1\text{-}Cp(CH_2)_3NMe\}Zr(NMe_2)_2$

$Cp(CH_2)_3NHMe$ and $\{\eta^5{:}\eta^1\text{-}Cp(CH_2)_3NMe\}Zr(NMe_2)_2$ were synthesized by a modification of literature methods [23]. A solution of 2 M NaCp (1 L, 2.0 mol) was added dropwise to $BrCH_2CH_2CH_2N(H)Me\cdot HBr$ (232 g, 1 mol) dissolved in 1.3 L of THF at 0 °C. Upon completion of the addition, the reaction mixture was warmed to room temperature and stirred for 12 h. After the filtration, all volatile species were removed by evaporation, which left the crude $Cp(CH_2)_3NHMe$. The pure product (89 g, 65%), a clean pale yellow liquid, was obtained by fractional distillation. ^1H NMR (300 MHz, $CDCl_3$) δ 6.02–6.43 (m, 3H), 2.89–2.95 (m, 2H) 2.59 (m, 2H), 2.35–2.43 (m, 5H), 1.75 (m, 2H), 1.26 (br s, 1H).

A flame-dried 3-L Schlenk flask was charged with toluene. $Zr(NMe_2)_4$ (15.6 g, 58.4 mmol) was added and dissolved, and the solution was cooled to −20 °C. A solution of $Cp(CH_2)_3NHMe$ (8.02 g, 58.4 mmol) in toluene (25 mL) was added dropwise. Upon completion of the addition, the reaction mixture was warmed to 40 °C. After being stirred for 15 m, the toluene solvent was removed under reduced pressure to give the crude $\{\eta^5{:}\eta^1\text{-}Cp(CH_2)_3NMe\}Zr(NMe_2)_2$. The product (17.38 g, 90%), a yellow oil, was received by fractional distillation. ^1H NMR (300 MHz, C_6D_6) δ 5.95 (t, 2H), 5.76 (t, 2H), 3.21 (s, 3H), 2.91 (s, 12H), 2.76 (m, 2H), 2.50 (m, 2H), 1.79 (m, 2H).

2.3. Film growth and characterization

ZrO_2 thin films were deposited on an Si(100) substrate using a showerhead-type hot-wall ALD reactor, manufactured by ASM Geneteck, Inc. (Korea). The pressure during deposition was 133.3 Pa and the number of cycles of the source pulse was varied from 68 to 200 to control the thickness. A cycle consisted of a sequence of source (5 s)/purge (10 s)/O_3 (5 s)/purge (10 s). The ALD growth conditions are summarized in Table 1. Argon (>99.999%) and ozone were used as carrier and reactant gases, respectively. Here, O_3 was generated from O_2 (>99.999) in an ozne geneator (Ozonetech, AB-II). Before use, the p-type Si substrate (LG Siltron Inc., 2 × 2 cm) was washed with a H_2SO_4 and H_2O mixed solvent (volume ratio = 3:1) for 10 min and then rinsed in deionized water. The substrate was then washed with a HF solution (vol% = 1) for 1 min and then rinsed in deionized water before loading into the reactor. The morphology of the film was studied with a Tecnai G2 F30 transmission electron microscope (TEM) operated at 300 kV and the thickness was evaluated from the TEM image. Film morphology and roughness were also measured by atomic force microscopy (AFM). The crystallinity of the film was investigated by grazing