



Atomic layer deposition of an HfO₂ thin film using Hf(O-iPr)₄

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ABSTRACT

A thin film of hafnium dioxide (HfO₂) was formed on the surface of Si(100) by atomic layer deposition (ALD) using Hf(O-iPr)₄ (Hf(OCH(CH₃)₂)₄, hafnium tetrakis-iso-propoxide) as an Hf source and O₂ as an oxidant. The temperature window of the process was 250–350 °C, which is about 100 °C lower than that of a process using Hf(O-tBu)₄ as a source. This result was in accordance with the decomposition characteristics of the Hf precursor, as investigated by the temperature-programmed decomposition of the compound in an ultra-high vacuum and by thermogravimetric analysis in air. The thickness of a film deposited under the above conditions increased in proportion to the ALD cycles, indicating that the film-growth rate per cycle remained nearly constant during the process. The deposited film consisted of a monoclinic crystal phase included in an amorphous matrix, which was confirmed by X-ray diffraction. The film showed an equivalent-oxide thickness (EOT) of 2.1 nm and a leakage current density of 8.9×10^{-6} A/cm² at –1 V. The leakage current was three orders of magnitude lower than that of SiO₂ with the same EOT.

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1. Introduction

Modern microelectronic technology has evolved based on the continued efforts to scale down Si-based memory devices to levels as low as sub-90 nm. However, the leakage of current through the ultra-thin film of the conventional gate SiO₂ in such small devices indicates the necessity of finding an alternative dielectric material [1].

HfO₂ is a viable candidate for gate dielectrics because it has a large band gap, thermal stability, mechanical strength, and is expected to form a stable thin film on silicon substrate [2,3].

Atomic layer deposition (ALD) is considered to be a promising method for obtaining a film of nanometer-scale thickness, which has good step coverage and thickness controllability [4]. In conventional metal-organic chemical vapor deposition (MOCVD), relatively high process temperatures are required to initiate reactions among the reactants. In the ALD process, however, the temperature is not necessarily so high because the reactants are independently decomposed in sequential steps [5]. ALD is also advantageous over MOCVD for forming a film of uniform thickness on the complicated contour of small devices [5].

So far, metal alkoxides together with oxidants have been used for preparing metal-oxide films by ALD. Typical alkoxides used were iso-propoxides and tert-butoxides. In the case of HfO₂ deposition, however, Hf(O-tBu)₄ instead of Hf(O-iPr)₄ was exclusively used [6] because the former is liquid at room temperature while the latter is a solid. Nevertheless, it is noteworthy that Hf(O-iPr)₄ is decomposed at lower temperatures than Hf(O-tBu)₄ [7] and therefore it is expected

that the temperature of the deposition process can be lowered by using the former instead of the latter as an Hf source.

Based on the above considerations, we attempted to form an HfO₂ film on Si(100) by ALD at relatively low temperatures by using Hf(O-iPr)₄ as an Hf precursor. The decomposition characteristics of the precursor were investigated using thermogravimetric analysis (TGA) and a temperature-programmed decomposition (TPD) method, and the information obtained was used for the selection of process conditions that would allow the ALD of HfO₂. Finally, the electrical properties of the prepared film were measured.

2. Experimental details

2.1. TGA and TPD of Hf(O-iPr)₄

The vaporization and thermal decomposition characteristics of Hf(O-iPr)₄·C₃H₇OH, purchased from Strem Co., were analyzed with a thermogravimetric analyzer (TG 2050, TA instruments), as the Hf compound was heated from 25 °C to 600 °C at a rate of 10 °C/min in a flowing air atmosphere.

The decomposition of the Hf compound, which had been adsorbed onto an Si(100) substrate, was also studied in an ultra-high vacuum (UHV), at pressures lower than 6.7×10^{-8} Pa, obtained using a turbomolecular pump (Varian Turbo-V701). Prior to being loaded in the UHV system, the Si(100) substrate was cleaned from surface hydrocarbons and native oxides by sequential dipping in Piranha (H₂O₂:H₂SO₄ = 3:7 at 120 °C, 10 min) and HF (HF:H₂O = 1:10 at 25 °C, 4 min) solutions. The surface of the Si(100) substrate was additionally cleaned in an UHV chamber by Ar ion sputtering (2 keV, 1.3×10^{-4} Pa, 30 min), followed by annealing at 700 °C. Gaseous Hf compound,

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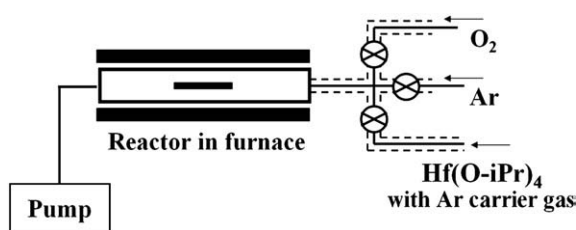


Fig. 1. Schematic diagram of the experimental unit used for ALD. The gas lines were heated to 170 °C to prevent the condensation of $\text{Hf}(\text{O-iPr})_4$ vapor in the lines.

obtained by vaporizing the liquid precursor at 160 °C, was introduced into the UHV chamber so as to be adsorbed onto the Si(100) substrate. Chemical species desorbed from the substrate surface were analyzed using a quadrupole mass spectrometer (QMS, Balzers QMS 200M) as the substrate was heated from -120 °C to 700 °C at a rate of 0.5 °C/s.

2.2. Atomic layer deposition

Atomic layer deposition was conducted using a home-made, hot-wall and travelling-wave type deposition chamber, as shown in Fig. 1. p-Type Si(100) (2 cm × 3 cm) substrate was cleaned by the same method as that used for the TPD experiments. The compound was pre-heated at 120 °C for 1 h to eliminate the additional amounts of free isopropyl alcohol, $\text{C}_3\text{H}_7\text{OH}$, before being vaporized at 160 °C in an Ar flow. The chamber pressure was kept at 4.0×10^2 Pa during the experiments carried out at temperatures between 150 °C and 500 °C. A fixed pulse time, which was selected based on the experimental results (see Section 3.2), was used for sequentially flowing different gas streams into the chamber during the ALD process. The gas streams were $\text{Hf}(\text{O-iPr})_4$ vapor diluted in an Ar carrier, pure Ar for removing excessively adsorbed $\text{Hf}(\text{O-iPr})_4$ from the substrate, and O_2 for oxidizing the adsorbed $\text{Hf}(\text{O-iPr})_4$. During the intervals between the gas flow, the chamber was evacuated to 1.3 Pa. The time schedule of the ALD process is described in Fig. 2. The thickness of the deposited thin film was measured using an ellipsometer (Auto Gain Ellipsometer L116B, Gaertner).

2.3. Composition and electrical properties of deposited thin film

The composition of the deposited film was analyzed using a scanning Auger microprobe system (cylindrical mirror analyzer, Model 660, Perkin-Elmer, emission current: 3 μA , accelerating voltage: 5 kV) and X-ray diffraction (XRD, Model M18XHF-SRA, Mac-Science Co., radiation source: $\text{CuK}\alpha$, scan rate: 2 °/min).

A metal–insulator–semiconductor (MIS) type capacitor was prepared by depositing circular Pt electrode dots, using an electron-beam evaporation method, on the Hf oxide film formed by ALD. The area of the

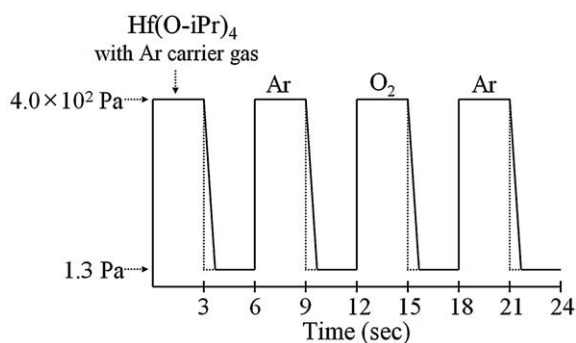


Fig. 2. Sequences of individual steps in the ALD process to obtain an HfO_2 film using $\text{Hf}(\text{O-iPr})_4$ and O_2 . Temperatures were the same for individual steps. Gases were introduced into the deposition chamber at 4.0×10^2 Pa.

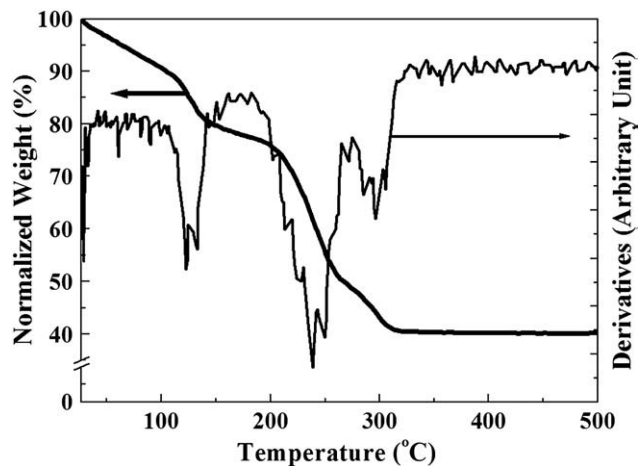


Fig. 3. TGA of $\text{Hf}(\text{O-iPr})_4$ and the first derivative of the result. The heating rate was 5 °C/min.

Pt electrode was 6.25 mm². The capacitance–voltage (C–V) information of the deposited film was measured using a system consisting of a probe station (MM-410C12, Micromanipulator Co.) and a plotter (HP4280A, Hewlett-Packard). The current–voltage curve was obtained using a system consisting of a probe station (REL-3200, Cascade Microtech) and a current analyzer (HP4155A, Hewlett-Packard).

3. Results and discussion

3.1. Vaporization and decomposition of $\text{Hf}(\text{O-iPr})_4$

Fig. 3 shows that the Hf precursor compound continues to lose its weight above room temperature, particularly at a significant rate near 120 °C. This is believed to originate from the dissociation of isopropyl alcohol, $\text{C}_3\text{H}_7\text{OH}$, which was included in the purchased compound as a weakly-bound species. A similar phenomenon was reported for $\text{Zr}(\text{O-iPr})_4$, which also contained isopropyl alcohol that had been incorporated into the compound during a synthesis process [8]. According to Fig. 3, $\text{Hf}(\text{O-iPr})_4$ started to vaporize at 210 °C and was decomposed at about 250 °C, but the weight remained nearly unchanged above 300 °C. The residue obtained at the end of the TGA was HfO_2 according to analysis by inductively coupled plasma-atomic emission spectroscopy. The residual weight corresponded to 43% of the initial weight, which was close to the theoretical value of 44% obtained by assuming that the sample compound was $\text{Hf}(\text{O-iPr})_4 \cdot \text{C}_3\text{H}_7\text{OH}$.

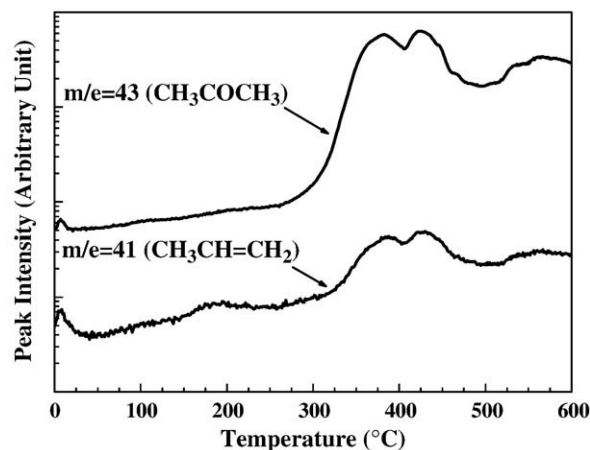


Fig. 4. The UHV-TPD of $\text{Hf}(\text{O-iPr})_4$ on Si(100).

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