

Research Paper

The Effects of Thermal Decomposition of Tetrakis-ethylmethylaminohafnium (TEMAHf) Precursors on HfO₂ Film Growth using Atomic Layer Deposition

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Abstract The ALD process is an adequate technique to meet the requirements that come with the downscaling of semiconductor devices. To obtain thin films of the desired standard, it is essential to understand the thermal decomposition properties of the precursors. As such, this study examined the thermal decomposition properties of TEMAHf precursors and its effect on the formation of HfO₂ thin films. FT-IR experiments were performed before deposition in order to analyze the thermal decomposition properties of the precursors. The measurements were taken in the range of 135°C-350°C. At temperatures higher than 300°C, there was a rapid decrease in the absorption peaks arising from vibration of Sp³ C-H stretching. This showed that the precursors experienced rapid decomposition at around 275°C- 300°C. HfO₂ thin films were successfully deposited by Atomic Layer Deposition (ALD) at 50°C intervals between 150°C to 400°C; the deposited films were characterized using a reflectometer, X-ray photoelectron spectroscopy (XPS), Grazing Incidence X-ray Diffraction (GIXRD), and atomic force microscopy (AFM). The results illustrate the relationship between the thermal decomposition temperature of TEMAHf and properties of thin films.

Keywords: Atomic Layer Deposition, HfO₂, FT-IR, TEMAHf, Thermal decomposition

I. Introduction

With the continuous downscaling of complementary metal oxide semiconductor (CMOS), high dielectric constant (high-k) materials have been used in MOS devices. Among the high-k materials, HfO₂ has commonly been used in many industries due to its high relative permittivity [1] and its stability in contact with silicon [1].

Various methods of fabricating HfO₂ thin films, such as Atomic Layer Deposition (ALD) [2], Metal-Organic Chemical Vapor Deposition (MOCVD)[3], and Metal-Organic Molecular Beam Epitaxy(MOMBE)[4], have been used.

Among these methods, ALD is a desirable deposition method for the downscaling of metal oxide semiconductors. ALD can offer various advantages such as excellent uniformity, accurate thickness control down to nanoscale size, and more uniform films [5]. So, ALD processes have become popular for the fabrication of HfO₂ thin films. Among various precursors of HfO₂ thin films, Tetrakis (ethylmethylaminohafnium) [TEMAHf] has primarily been used in the ALD process due to its relatively high vapor

pressure, thermal stability on Si-wafer, and weak metal-nitrogen bonding; TEMAHf can be used to fabricate metal-oxide films with a higher purity level [6]. Accordingly, precursor choice is important. Another factor as important as the choice of precursors is the effect of the thermal decomposition properties on the deposited films. The ALD process deposits thin films based on a gas phase chemical process involving reactions with oxidizing agents in a self-limiting manner. Thermal decomposition occurs when gas phase precursors are deposited on substrates and solid oxides are produced. An understanding of the effects of the thermal decomposition on thin films is necessary in order to obtain thin films of high quality. However, few studies exist on this subject. In this work, in order to determine the relationship between the precursor decomposition and the films properties, an analysis of the thermal decomposition properties of TEMAHf and of the deposited films has been performed. Using Fourier transform infrared spectroscopy (FT-IR), we performed real time observations of the gas phase of the TEMAHf decomposition process under variation of temperature from 135°C to 350°C. Then, for substrate temperatures in the range of 150-400°C, the properties of the films deposited using ALD were analyzed by X-ray photoelectron spectroscopy (XPS), grazing incidence X-ray diffraction (GIXRD), and atomic force microscopy (AFM).

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II. Experiment

1. Gas phase analysis

FT-IR research was performed in order to identify the thermal decomposition of the heated precursor TEMAHf. A heated canister and the FT-IR apparatus were connected to analyze the decomposition property in real time. The temperatures of the precursor canister and the transport line were fixed at 60°C; Ar carrier gas was flowed through the line. The vacuum chamber for FT-IR was heated from 135°C to 350°C. As the temperature increased, an FT-IR peak was observed; it was measured and found to be in the 1600-4000cm⁻¹ wave number region.

2. ALD process

For the ALD process, we used Si wafers with resistivity values in the range of 0.001-0.003 Ω. Prior to the deposition process, the Si wafer was subjected to RCA cleaning and put into dilute HF solution (50:1, D.I. water) to remove native Si oxide. Then, the cleaned Si wafers were put into a reactor for 30 min so that they would attain thermal stability. The prepared HfO₂ films were deposited using the ALD reactor. The ALD cycle used Hf precursors (TEMAHf, Up Chemical (99.99%)) pulsed with carrier gas, Ar gas flow rate of 70 standard cubic centimeters per minute (SCCM), and O₃ reactant, which was pulsed on the substrate. Each process was conducted for 300 cycles. To obtain an ALD window region, thin films were deposited at different substrate temperatures of 150°C, 200°C, 250°C, 300°C, 350°C, and 400°C; source temperature was fixed at 60°C for TEMAHf.

Each step was as in the following. TEMAHf for 0.5 s with carrier gas for 4.5 s was exposed to the surface. Subsequently, to remove physical adsorption, Ar was purge into surface for 10s and then, oxidant O₃ was exposed into surface for 1.2 s to make HfO₂ chemical bonding. Finally, to eliminate subsistant physical adsorption, Ar was purged into surface for 10s. This 1 cycle was repeated for 300cycles to make HfO₂ thin films.

3. Properties of thin films

The characteristics of the deposited thin films were analyzed by XPS (Multi Purpose X-Ray Photoelectron Spectroscopy) to identify chemical bonding; GIXRD (grazing incidence X-ray diffraction, radian: CuKα1, lambda: 1.54056) was used to determine the crystalline properties; surface roughness of the thin films was acquired using AFM (Atomic Force Microscope). AFM cantilever mode was used as non-contact mode. Finally, the thickness of the HfO₂ thin films was measured using a reflectometer (ST2000-DLXn, K-MAC).

III. Results and Discussion

Fig. 1 shows the results of the FT-IR analysis for the

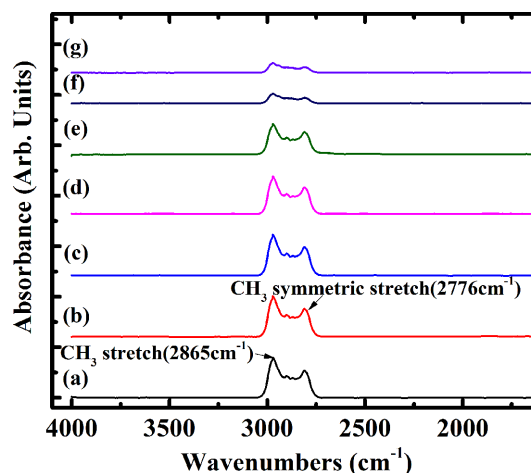


Figure 1. FT-IR spectra of TEMAHf at heating temperatures: (a) 135°C, (b) 145°C, (c) 165°C, (d) 245°C (e) 275°C, (f) 300°C, and (g) 350°C.

TEMAHf precursors. The temperature range shown in Fig. 1(a)-(g) is from 135°C to 350°C. As the temperature rises, there is a decrease in the Sp³ CH₃ stretching peak (2865 cm⁻¹) and in the CH₃ symmetric stretching (2776 cm⁻¹). This is due to the CH₃ deformation such as asymmetric bonding of CH₃ stretching vibration; the intensity decreases compared to those of the other CH_x peaks with greater decomposition at higher temperatures. In addition, the intensity declines rapidly when the temperature exceeds 300°C. This is consistent with that the kinetic energy of the C-containing species exceeds the activation energy at higher temperatures, resulting in the breaking of chemical bonds.

From the FT-IR spectra, this study found that the TEMAHf precursors undergo rapid decomposition between 275°C and 300°C. The actual ALD process was used to determine the effects of the thermal decomposition temperature on the thin films. Fig. 2 shows the thickness of the thin films in relation to the substrate temperature in the range of 150°C to 400°C. In the graph, it can be seen that the ALD window of the deposited films occurred between 200°C and 300°C. The Growth Per Cycle (GPC) values were measured and found to be 0.103, 0.1, 0.08, 0.09, 0.13, and 0.33 nm at 150, 200, 250, 300, 350, and 400°C respectively. These measurements coincide with the previously reported ALD window of TEMAHf+O₃ and the rapid increase in thickness at temperatures exceeding 370°C [9]. Due to the rapid thermal decomposition of the precursors from 350°C onwards, the thickness tends to deviate from values attained during the ALD window. This corresponds to the beginning of precursor decomposition at temperatures higher than 300°C, as demonstrated through FT-IR, and to the beginning of a gradual increase in thickness.

Fig. 3 shows the XPS spectra of thin films deposited at various substrate temperatures. Fig. 3(a) shows Hf 4f chemical state in relation to the temperature of the thin films. Hf-O bonding can be observed for Hf 4f_{7/2} and Hf

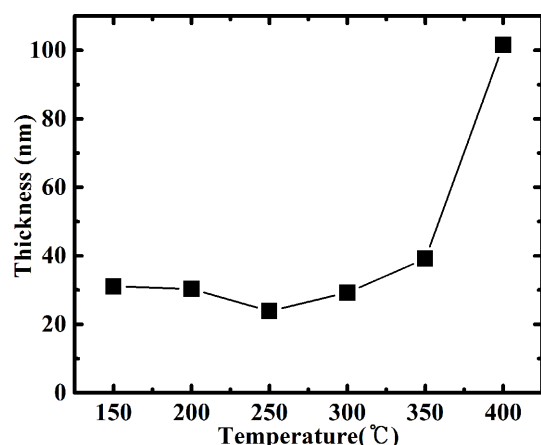


Figure 2. Thickness of the HfO₂ thin films grown at various substrate temperatures.

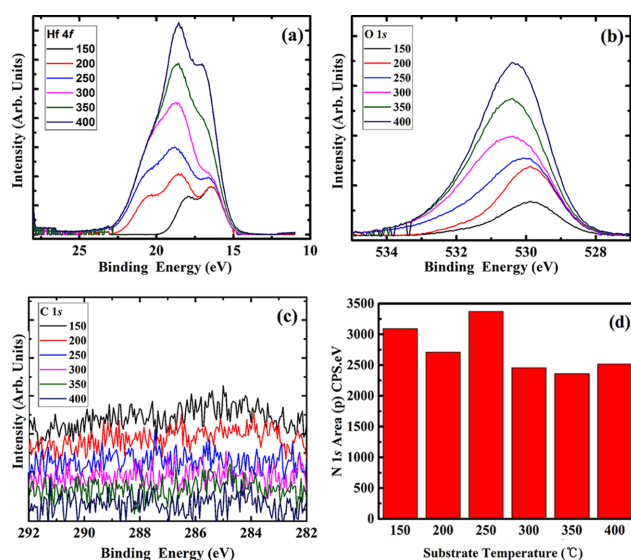


Figure 3. XPS spectra of the nanocrystalline HfO₂ films deposited at various substrate temperatures: (a) Hf 4f, (b) O 1s, (c) C 1s, and (d) N 1s peak.

$4f_{5/2}$ at 16.7 eV and 18.2 eV, respectively [8]. However, the films deposited at 150°C did not fulfill the stoichiometric coefficients of HfO₂. This negative result can be traced to the lack of chemical bonding between TEMAHf and O₃ due to the insufficient substrate temperature. From 200°C, which falls in the ALD window, chemical shifting occurs and the binding energy becomes fixed at 18.2 eV (Hf4f_{5/2}). This indicates that Hf is in the +4 oxidation state and is engaged in the HfO₂ bonds [8]. Hf-Si bonds, usually observed at 14–16 eV, could not be found. Fig. 3(b) shows the binding energy of O 1s. In a past study, the O 1s chemical state shift of HfO₂ films was examined in relation to film thickness [9]. This study also observed chemical state shifts in relation to the temperature of the substrates, which are involved in the thermal decomposition of the precursors. Table 1 shows the relationship between the substrate temperature and the thickness. O 1s chemical state shifts were observed to be related to the thickness. The O 1s binding energy values of the films deposited at 150°C–

Table 1. Experimental measurement values at various substrate temperatures.

Sub.temp (°C)	Cycle numbers	Thickness (nm)	GPC (nm)	rms (nm)	rms/thickness
150	300	31.065	0.1036	0.152	0.0049
200	300	30.33	0.1011	0.161	0.0053
250	300	23.869	0.0796	0.174	0.0073
300	300	29.25	0.0975	2.288	0.0782
350	300	39.13	0.1304	2.436	0.0623
400	300	101.493	0.3383	1.618	0.0159

400°C were 529.88, 529.91, 531.14, 531.07, 530.46, and 530.12. Comparing these results to the thickness values shown in Table 1, we can see that a higher binding energy is obtained at smaller thickness. However, films deposited at 350°C and 400°C did not exhibit the same tendencies as those deposited at 150°C and 250°C. From the above, it can be deduced that the thermal decomposition temperature of TEMAHf influences the O 1s chemical state shifts of HfO₂ films.

Through the XPS data, we were able to determine the effects of impurities in the thin films in relation to the thermal decomposition temperature of the precursors. Fig. 3(c) shows the XPS spectra of C 1s in relation to the substrate temperature. The residual C impurities of the deposited films have fewer constituents, but the carbon component still remained in the films deposited at low temperatures. This corresponds to the results of past research [10]. The breaking of chemical bonds did not occur due to the lack of heat energy at the relatively lower deposition temperature on the substrate surface. Because the kinetic energy exceeds the activation energy with increasing deposition temperature, fewer C impurities remain in the thin films, and the broken chemical bonds are presumed to have moved to the exhaust pipe. The presence of C impurities on the deposited films can be explained by the following. The heat energy breaks down the C-H bonds, and the residual C has an unpaired electron. This unpaired electron becomes strongly bonded to the substrate and cannot easily be removed. Moreover, further oxidization takes place due to the half-reaction of O₃ [10].

Fig. 3(d) shows the N 1s peak area. There is a decrease of N 1s peak area in Hf-N bonds in thin films deposited after 250°C. From this, we can deduce that the Hf-N bonds of TEMAHf were broken down in the range of 250°C–300°C. N-C bonds can also be broken because of not only the influence of Hf-N scission but also the strong oxidizing nature of O₃. By-products such as N₂O and NO, produced from oxidation after the breaking of chemical bonds, may result in residual N impurities [10].

Fig. 4 shows the GIXRD patterns of films deposited at various temperatures. Regardless of the deposition temperature, the films exhibited a monoclinic structure. The GIXRD graphs were similar for all films at 150, 200, 250, and 300°C, with a (202), (130) monoclinic structure.

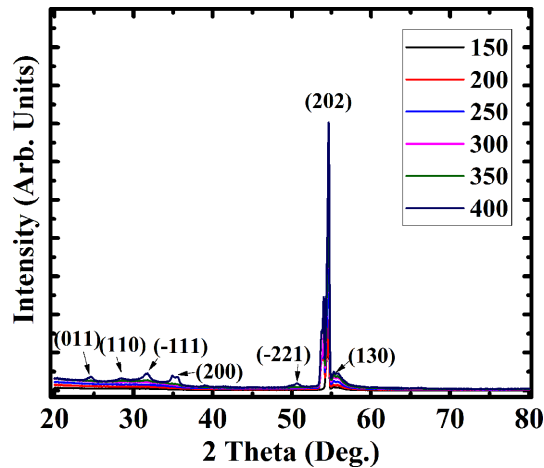


Figure 4. GIXRD patterns of the HfO₂ films deposited at various substrate temperatures.

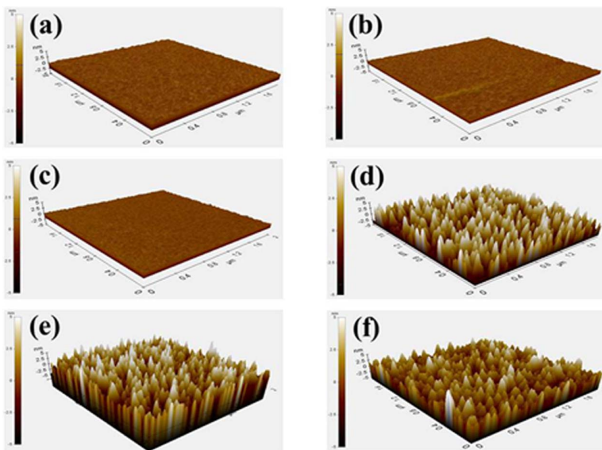


Figure 5. AFM images of HfO₂ thin films deposited at (a) 150°C, (b) 200°C, (c) 250°C, (d) 300°C, (e) 350°C, and (f) 400°C.

A preferential orientation of (202) was observed for all deposition temperatures. The intensity of the (130) structure increased significantly compared to the intensity before 300°C. From 350°C onwards, (011), (110), (-111), and (200) structures were observed. Crystallization progressed to a greater degree for the thin films deposited at 350°C, and peaks that were not observed in films deposited up to 200°C were found. This implies that the crystalline structure is affected by the deposition temperature. In a past study, the ALD process was performed using TEMAHf and O₃ at a substrate temperature of 330°C. Crystallization did not occur significantly at 330°C, thus corresponding to the results of the present study [7]. The greater crystallization at higher substrate temperatures ($\geq 350^\circ\text{C}$) is caused by the movement of atoms to positions of higher stability. However, depending on the type of precursor, the degree of crystallization changes even at the same deposition temperature [7]. A past study showed that the same metal-based precursors can have different crystallization, preferential orientation, volatility, and thermal stability depending on the type of ligand [7]. Accordingly, it can be deduced that crystallization is influenced by the thermal properties of the precursors.

Fig. 5 shows the surface roughness of the films deposited at various temperatures. The deposited films were measured using the non-contact mode and zoomed to a size of 2 μm X 2 μm . Fig. 5(a)-(f) present 3D images of the films deposited in the range of 150-400°C. The rms roughness values were 0.152 nm at 150°C, 0.161 nm at 200°C, 0.174 nm at 250°C, 2.288 nm at 300°C, 2.436 nm at 350°C, and 1.618 nm at 400°C. The roughness increased to 350°C with increasing temperature. The level of rms increase also grew larger from 300°C. At 400°C, however, the rms began to decrease. The rms values were divided by thickness (rms/thickness), and the results are given in Table 1. In a past study, the roughness of HfO₂ thin films deposited at 400°C, 450°C, and 500°C was measured using the same method [7]. Similar to the results of the present study, rms/thickness values decreased with increasing deposition rate. Different tendencies were observed from 250°C to 300°C. The results were similar from 150°C to 250°C and from 300°C to 400°C, but not between 250°C and 300°C. From this, it can be deduced that the differences result from the thermal decomposition of metal sources between 250°C and 300°C.

IV. Conclusions

FT-IR was employed to analyze the thermal decomposition properties of TEMAHf. HfO₂ thin films were deposited by the ALD method using TEMAHf and O₃. The FT-IR analysis showed that the precursors experienced rapid decomposition in the temperature range of 275°C-300°C. Deposition was performed at a substrate temperature range of 150°C-400°C. The ALD window was identified in the temperature range of 200°C- 300°C where the stoichiometric HfO₂ thin films were fabricated. The relationship between O1s chemical state shifts and the decomposition temperature of TEMAHf was deduced through the relationship between deposition temperature and thickness. By analyzing the residual impurities, the relationship between impurities and the thermal decomposition properties of TEMAHf was examined. The crystallinity of the thin films was found to differ with the substrate temperature, which was clearly related to the thermal decomposition properties of the precursors. RMS analysis and calculation of the rms/thickness revealed different tendencies in the range of 250°C- 300°C. These results prove that thin film properties are influenced by the thermal decomposition temperature of precursors.

V. Author Contributions

The first and second authors contributed equally to this work.

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