

Thermodynamic properties and interfacial layer characteristics of HfO₂ thin films deposited by plasma-enhanced atomic layer deposition

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(Received 8 December 2006; accepted 4 May 2007; published online 29 May 2007)

The thermodynamic properties and interfacial characteristics of HfO₂ thin films that were deposited by the direct plasma atomic layer deposition (DPALD) method are investigated. The as-deposited HfO₂ films that were deposited by the DPALD method show crystallization of the HfO₂ layers, which initiates at approximately the 35th cycle (about 2.8 nm) of the DPALD process. Medium-energy ion scattering analysis reveals that the direct O₂ plasma causes a compositional change in the interfacial layer as the process progresses. With an increase in the number of process cycles, the Si content decreases and the O content increases at that position, so that the HfO₂-like Hf-silicate layer is formed on top of the interfacial layer. The enhanced physical reactivity of the oxygen ions in the direct plasma and the Hf-silicate layer may be the driving forces that accelerate the early crystallization of the HfO₂ layer in the DPALD process in the as-deposited state. © 2007 American Institute of Physics. [DOI: 10.1063/1.2743749]

Many advanced semiconductor devices, in the integration progress of semiconductor fabricating processes, can be made with sub-0.1 μm technology. The International Technology Roadmap for Semiconductors (ITRS) of 2005 sets an equivalent oxide thickness (EOT) below 1 nm as one of the goals for the gate oxide of advanced semiconductor devices on the 2009 horizon.¹ Therefore, conventional SiO₂ gate stacks in metal oxide semiconductor field effect transistors are reaching physical and electrical limitations from the gate leakage current viewpoint.²

In order to overcome these limitations, high dielectric constant (high-*k*) materials have been studied extensively as alternative gate dielectrics. HfO₂ is one of the most promising candidates among the high-*k* materials because of its high dielectric constant ($k \sim 25$), wide band gap (~ 5.68 eV), and good thermodynamic stability when in contact with Si.³ However, the EOT value of the HfO₂ gate stack increases, due to the growth of an interfacial layer between HfO₂ and the Si substrate. Moreover, the HfO₂ layer must be crystallized at or below 500 °C.^{4,5} It is necessary to study how to control the interfacial layer and the thermal stability of the HfO₂ layer because of important device applications.

Moreover, a nanolevel thin film deposition method is necessary for the modern semiconductor manufacturing process. The atomic layer deposition (ALD) method has been widely studied, in which there are a variety of practical advantages including precise thickness control on the nanolevel for thin films, excellent step coverage, and uniform film properties over a large substrate area.⁶

In order to obtain high quality high-*k* films, it is important to control the thermodynamic properties of the film. In the case of HfO₂ deposition with a halogen precursor, HfCl₄, and H₂O using a general flow-type ALD reactor that does not use any plasma at 300 °C, the HfO₂ layer, excluding the

interfacial layer, with a thickness between 50 and ~ 100 Å, is altered to polycrystalline mixed with the monoclinic and tetragonal structures.⁷ However, deposition with a metal-organic (MO) precursor, tetrakis(ethylmethylamino)hafnium, and H₂O with the ALD method, the as-deposited HfO₂ 10 nm film shows an amorphous structure.⁸ As an example, MO precursors have several benefits in growing thin films compared with halogen precursors. However, the MO precursors have rather low film density and high impurity concentration. In order to solve these problems, the plasma-enhanced ALD (PEALD) method has been studied for the purpose of growing high-*k* thin films.⁹

Although the PEALD method has many deposition advantages for high-*k* thin films, the effect of plasma damage on the deposited high-*k* films and substrates, based on highly reactive chemical species in plasma, has not been extensively studied. In a previous report, a 3.1 nm thick HfO₂ film, excluding the interfacial layer, was deposited by using the direct plasma ALD (DPALD) process with tetrakisdiethylaminohafnium (TDEAH) and O₂ plasma. This film showed a polycrystalline structure in the as-deposited state, while an amorphous structure in a 2.3 nm thick HfO₂ film was revealed when a remote plasma ALD (RPALD) process was used. Moreover, the interfacial layer composition of the HfO₂ film on the DPALD is different from that in the RPALD process.¹⁰

In this study, there were two focus points, including: “when does the crystallization of a HfO₂ layer in the DPALD process occur?” and “what is the driving force of early crystallization in the DPALD process?” This study examined the thermodynamic properties and the interfacial layer characteristics of HfO₂ thin films deposited with the DPALD method. The crystallization initiation of the HfO₂ layers was determined and it was verified with medium-energy ion scattering (MEIS) analysis that a composition change occurred in the interfacial layer of the HfO₂ film as the number of process cycles increased in the DPALD method. From these

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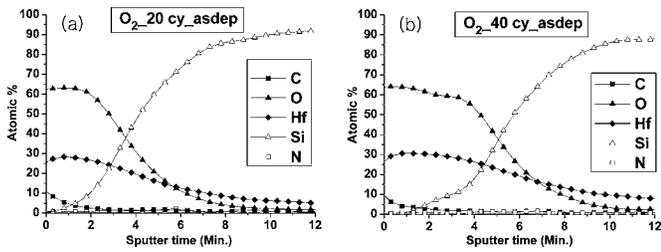


FIG. 1. AES depth profiles of (a) 20- and (b) 40-cycle HfO_2 films on a Si substrate using DPALD processes at a deposition temperature of 250°C using a $\text{Hf}(\text{NEt}_2)_4$ precursor and oxygen plasma.

results, the driving force of the HfO_2 crystallization was investigated.

The HfO_2 thin films were deposited on *p*-type Si (100) substrates with a resistivity in the range of $0.1\text{--}0.2\ \Omega\ \text{cm}$. The Si substrates were cleaned with a Piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2=4:1$) for 10 min and then with a dilute HF solution $\text{HF}:\text{H}_2\text{O}=1:100$ for 2 min to remove organic contaminants and native oxides, respectively. The MO hafnium precursor, TDEAH, was used and introduced into the ALD chamber via a bubbler using an argon carrier gas during the DPALD process. The oxygen reactant was produced during pulsing of the O_2 plasma. An argon purge gas was introduced for the complete separation of the precursor and reactant gas. The basic single cycle consisted of supplying the hafnium precursor and the oxygen plasma as a source and a reactant gas, respectively. During the HfO_2 deposition processes, the process pressure and substrate temperature were kept at 0.1 Torr and 250°C .

The thickness of the films was determined from cross sections using high-resolution transmission electron microscopy (HRTEM). The chemical composition of the as-deposited HfO_2 films was studied by using Auger electron spectroscopy (AES) and MEIS. The MEIS analysis was accomplished by using a 100 keV proton beam with double alignment that reduced contributions from the crystalline Si substrate and permitted the deconvolution of the spectra into contributions from the interfacial layer and the Si. The incident ions were directed along the Si (111) plane, and the scattered ions were directed along the Si (001) plane at a scattering angle of 125° .⁷ For a more detailed interpretation of the HfO_2 growth mechanism, the MEIS spectra were simulated using the KIDO program.¹¹

In order to confirm the film composition of the HfO_2 from the DPALD deposition method, AES analysis was carried out, as shown in Fig. 1. Both (a) 20- and (b) 40-cycle HfO_2 films show the HfO_2 stoichiometric characteristics and relatively constant compositional variations throughout the films. Each sample shows evidence of hafnium, oxygen, silicon, carbon, and nitrogen. The AES depth profiles show the composition of the HfO_2 film and show that there is no distinguishable composition change with further process cycles. The low impurity content (carbon and nitrogen) in the films, deposited by using the DPALD method, is caused by the complete separation of the precursor and the reactant gas by the Ar purge and the relatively high reactivity of the direct O_2 plasma.

Figure 2 shows HRTEM images of as-deposited HfO_2 thin film samples that were grown by (a) 30-, (b) 35-, and (c) 40-cycle DPALD processes. Based on the difference in the images, the thicknesses of the HfO_2 layers (excluding inter-

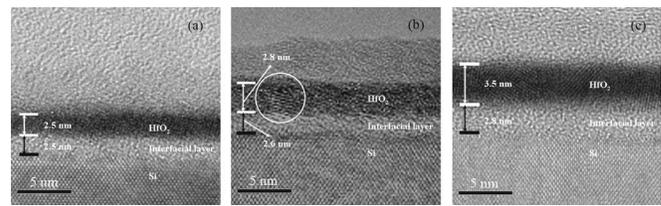


FIG. 2. Cross-sectional HRTEM images of as-deposited (a) 30-, (b) 35-, and (c) 40-cycle HfO_2 films on a Si substrate using the DPALD method.

facial layers) are 2.5, 2.8, and 3.5 nm, respectively, and those of the interfacial layers are 2.5, 2.6, and 2.8 nm, respectively. In Fig. 2(a) on the 30-cycle DPALD process, the HfO_2 layer shows an amorphous structure. However, the HfO_2 layer from the 35-cycle DPALD shows a partially crystallized structure [Fig. 2(b)], and a polycrystalline structure appears in the same layer on the 40-cycle DPALD process image [Fig. 2(c)]. It is thought that the crystallization of the HfO_2 layers, in case of the DPALD, started at around the 35-cycle DPALD process.

As mentioned in a previous study, it is considered that the HfO_2 crystallization in the DPALD sample was induced as the result of an enhanced physical reactivity of the oxygen ions in the plasma.¹⁰ However, there is cause to believe that there is one more reason related to the direct plasma that creates a rather large difference in the crystallization structure. This will be interpreted later as a result of MEIS analysis.

Figure 3 includes HRTEM and MEIS data taken from as-deposited HfO_2 thin films grown by 20- and 40-cycle

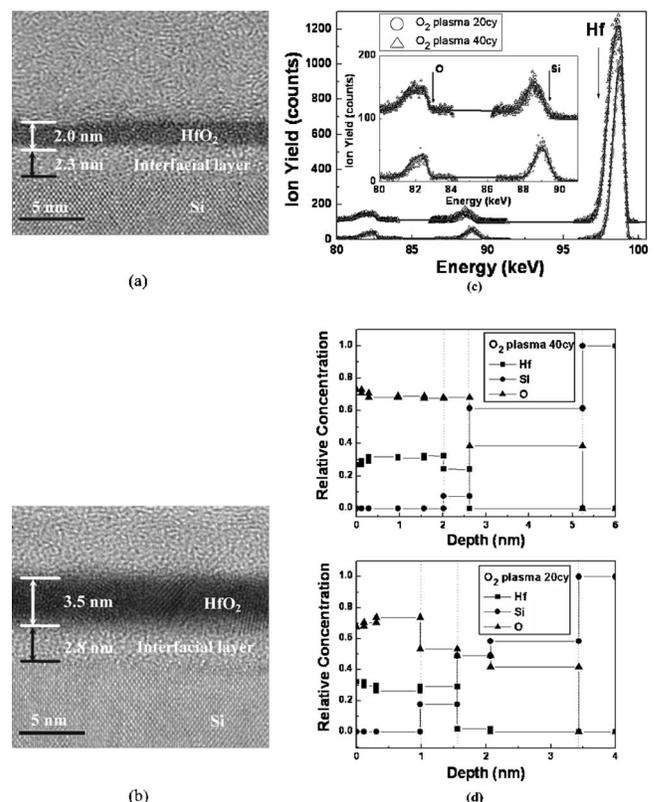


FIG. 3. HRTEM images for as-deposited (a) 20- and (b) 40-cycle DPALD HfO_2 thin films and their MEIS results: (c) open circles and open triangles represent raw data and solid lines represent fitted data. (d) The calculated relative concentration in the depth direction of the films from the fitting results.

DPALD processes. These images and data enable a detailed study of the stoichiometry and the compositional change in the interfacial layers as the number of process cycles increase and the layer thickness changes in the depth direction. The spectra of the Hf, Si, and O peaks from the two samples in Fig. 3(c) indicate that they are in different states, according to the DPALD process cycles. First, the Hf peak of the 40-cycle DPALD is wider by about 1.5 times than the 20-cycle DPALD, which means that the thickness of the former is thicker by about 1.5 times than the latter. This matches the HRTEM data of Figs. 3(a) and 3(b). The Si peak of the 40-cycle process is shifted toward a lower energy than the 20-cycle peak [shown in the inset of Fig. 3(c)]. It is thought that the Si peak shift is deeply related to the thicknesses of the HfO₂ films. During MEIS a beam causes ion scattering in a thin film, which is interpreted as the thicker the film, the bigger the energy loss of the beam. As a result, the Si peak taken from the substrate on the 40-cycle DPALD process was shifted toward a “lower” energy.

Figure 3(d) is the result of the calculated relative concentration in the depth direction of the interfacial layers taken from 20- and 40-cycle DPALD samples. It gives important information about the stoichiometry and the compositional change in the interfacial layer as the number of process cycles increases. Due to a thicker SiO_x composition in the 40-cycle process than in the 20-cycle process, the two interfacial layers show different film thicknesses, which match the HRTEM data in Figs. 3(a) and 3(b). Nevertheless, the two interfacial layer edges in contact with the HfO₂ layers in each DPALD sample have relatively the same thickness, that is, about 0.6 nm. Through the previous study, it was known that a Hf-rich silicate layer is formed in the DPALD process, while a Si-rich silicate layer is produced in the RPALD process.¹⁰ Both interfacial layer edges show a Hf-rich silicate structure. However, the concentration ratio of Si and O at the edge changes along with the number of process cycles. When the number of process cycles increases, the Si content decreases and O content increases in that position, while the Hf content does not show any distinguishable change. In addition, it can be thought that the earlier HfO₂ crystallization by direct plasma can easily roughen the interface through the formation of grains, and this would appear in MEIS as a change interface composition. Anyway, considering this result, the composition of the interfacial layer edge becomes more of a HfO₂-like Hf-silicate layer. In the heteroepitaxy process, for example, the existence of a buffer layer between a substrate and a certain layer can easily drive the crystalline growth of the target layer, which is grown onto the buffer layer.¹² This indicates that the HfO₂-like Hf-silicate edge function acts as the buffer layer

that initiates growth in the heteroepitaxy layer, and accelerates the early crystallization of the HfO₂ layer with the direct plasma in the DPALD process.

In conclusion, the crystal structure and interfacial layer edge property of HfO₂ thin films deposited by the plasma-enhanced atomic layer deposition method have been studied. The as-deposited HfO₂ layer taken from the DPALD samples reveals the crystallization of the HfO₂ layers, which is initiated around the 35th cycle (about 2.8 nm) of the DPALD process. MEIS analysis indicates that the O₂ direct plasma adapted into the DPALD process can make a HfO₂-like Hf-silicate layer edge that is in contact with a HfO₂ layer, as the number of process cycles increases. The Si peak of the 40 cycle is shifted toward a lower energy than the 20-cycle DPALD peak, in the MEIS data under the influence of the energy loss of the MEIS beam, in accordance with the increase of the HfO₂ interfacial layer. Moreover, increasing the number of process cycles causes a Si content to decrease and an O content to increase in that position, while the Hf content does not show any distinguishable change. This indicates that the HfO₂-like Hf-silicate layer edge is formed on the top of the interfacial layer. The enhanced physical reactivity of the oxygen ions in the direct plasma and the HfO₂-like Hf-silicate layer edge may be the driving forces that accelerate the crystallization of the HfO₂ layer in the as-deposited state of the DPALD process.

This study was supported by the National Program for Tera-level Nano-devices of the Ministry of Science and Technology as one of the 21st Century Frontier Programs.

¹International Roadmap for Semiconductors 2005 Process Integration, Devices and Structures.

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