Temperature-Dependent HfO$_2$/Si Interface Structural Evolution and its Mechanism

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Abstract

In this work, hafnium oxide (HfO$_2$) thin films are deposited on p-type Si substrates by remote plasma atomic layer deposition on p-type Si at 250 °C, followed by a rapid thermal annealing in nitrogen. Effect of post-annealing temperature on the crystallization of HfO$_2$ films and HfO$_2$/Si interfaces is investigated. The crystallization of the HfO$_2$ films and HfO$_2$/Si interface is studied by field emission transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and atomic force microscopy. The experimental results show that during annealing, the oxygen diffuse from HfO$_2$ to Si interface. For annealing temperature below 400 °C, the HfO$_2$ film and interfacial layer are amorphous, and the latter consists of HfO$_2$ and silicon dioxide (SiO$_2$). At annealing temperature of 450-550 °C, the HfO$_2$ film become multiphase polycrystalline, and a crystalline SiO$_2$ is found at the interface. Finally, at annealing temperature beyond 550 °C, the HfO$_2$ film is dominated by single-phase polycrystalline, and the interfacial layer is completely transformed to crystalline SiO$_2$.

Keywords: Hafnium oxide, Atomic layer deposition, Interface, Annealing, Crystallization

Introduction

Hafnium oxide (HfO$_2$) thin film is an interesting material for a variety of applications. It can be used in multilayer optical coating [1], protective coating [2], gate dielectric [3], passivating layer [4–6], and so on due to its excellent properties, such as high density, high refractive index, wide band gap, and relatively high thermal stability. Many methods have been used to prepare HfO$_2$ thin film, such as electron beam evaporation [7], chemical solution deposition [8], reactive sputtering [9], metal organic chemical vapor deposition [10], molecular beam epitaxy [11], and atomic layer deposition (ALD). ALD is a promising method for obtaining thin films with both high-precision thickness control and high accuracy uniformity. Post-annealing is found to have significant influences on ALD HfO$_2$ films [12–15]. According to the research, HfO$_2$ thin films can crystallize for an annealing temperature higher than 500 °C [16–18]. The crystalline structure of HfO$_2$ strongly affects optical and electrical properties. For example, the structural change of HfO$_2$ from amorphous to monoclinic crystalline phase could lead to changes of refractive index from 1.7 to 2.09, optical gap from 5.75 to 6.13 eV, and dielectric constant from 24.5 to 14.49 [19, 20]. For ALD HfO$_2$ deposited on silicon substrates, an oxide layer is usually observed at HfO$_2$/Si interface [21, 22]. The presence of this interfacial layer is reported to decrease the dielectric constant [22]. In addition, Kopani et al. [23] presented the structural properties of 5-nm HfO$_2$ films after nitric acid oxidation of n-doped Si substrates. They found that high annealing temperature increases the growth rate of crystalline nuclei. However, their crystallization properties particularly HfO$_2$/substrate interface have scantily been studied. Therefore, the annealing temperature affecting the crystallization properties of HfO$_2$ thin films prepared by ALD was worth for further investigation.

In this work, the HfO$_2$ thin films were fabricated by a remote plasma atomic layer deposition (RP-ALD) on p-type silicon substrates. Post-annealing was performed by a rapid thermal annealing (RTA) system at different temperatures. The structural changes and crystallization properties of HfO$_2$ thin films by RTA were characterized by atomic force microscopy (AFM), grazing incident X-ray diffraction (GIXRD), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). The crystallization behavior of HfO$_2$ thin films was investigated as a function of post-annealing temperature.
(XPS), and high-resolution transmission electron microscopy (HR-TEM). The temperature-dependent HfO₂/Si interface structural evolution and its mechanism are also investigated.

**Method**

Doubled-sided polished (100) oriented p-type 2-inch 250-µm Czochralski Si wafers with a resistivity of 30 Ω cm were used. Prior to the deposition, Si wafers were cleaned by a standard Radio Corporation of America method followed by dipping in diluted hydrofluoric acid solution (5%) for 2 min to remove possible stray oxides without final water rinse. After cleaning, all of the wafers were dried with pure nitrogen (N₂) gas and mounted onto the substrate holder. Approximately 15 nm HfO₂ (168 ALD cycles) thin films were deposited on Si wafers by RP-ALD (Picusun R-200, Finland) using tetrakis (ethylmethylamino) hafnium (TEMAH) and oxygen (O₂) in alternating pulse with N₂ purge of the reaction chamber between pulses. The TEMAH and O₂ plasma were pulsed into the reactor in the following sequence: TEMAH pulse 1.6 s; N₂ purge 10 s; O₂ plasma pulse 10 s, and N₂ purge 12 s. After depositing the HfO₂ thin films, the rapid thermal annealing was performed in N₂ ambient for 10 min. The annealing temperatures were varied from 400 to 600 °C to investigate the effect on crystallization of the HfO₂ thin films. The orthorhombic HfO₂ dominates the crystalline structure at higher annealing temperatures. However, the diffraction peaks of orthorhombic HfO₂ were observed at a lower 1/d (a smaller d-spacing) as compared to that in the ICDD PDF#21-0904. Other peaks near 1/d = 0.340 Å⁻¹ towards a higher value indicates that the monoclinic plane (ICDD PDF#34-0104, space group P2₁/c), respectively. The peak at 1/d = 0.340 Å⁻¹ corresponds to the (111) plane of the orthorhombic phase (ICDD PDF#21-0904, space group Pbcn). Other peaks near 1/d = 0.380–0.395 are the 200, 020, and 002 planes of the monoclinic and the 020 plane of the orthorhombic phases. The results also reveal that the monoclinic phase decrease and the orthorhombic phases increase with the annealing temperature. The orthorhombic HfO₂ dominates the crystalline structure at higher annealing temperatures. However, the diffraction peaks of orthorhombic HfO₂ were observed at a lower 1/d (a smaller d-spacing) as compared to that in the ICDD PDF#21-0904. In addition, the shift of 1/d = 0.340 Å⁻¹ towards a higher value indicates that the d-spacing decreases with the annealing temperature.

The concentrations of Hf and O within the HfO₂ films were measured using depth profiled XPS. Figure 3 shows the O/Hf composition ratio of the as-deposited and post-annealed HfO₂ films. The O/Hf ratio decreases from 1.60 to 1.29 with the annealing temperature. Due to the use of N₂ during the annealing, the HfO₂ becomes oxygen deficient with the temperature. The oxygen

| Parameter | Value |
|-----------|-------|
| Substrate temperature (°C) | 250 |
| TEMAH pulse time (s) | 1.6 |
| O₂ plasma pulse time (s) | 10 |
| O₂ plasma power (W) | 2500 |
| Thickness (nm) | 15 |
| RTA-post annealing process | Value |
| Temperature (°C) | 400–600 |
| Time (min) | 20 |
| Ambient | N₂ |
deficient HfO₂ film also results a smaller d-spacing as mentioned previously.

Figure 4a, b, c, d, e, and f show the high-resolution cross-sectional HR-TEM images of as-deposited 400 °C-, 450 °C-, 500 °C-, 550 °C-, and 600 °C-annealed HfO₂ thin films on Si substrates, respectively. It can be seen that the HfO₂ layer and Si substrate are clearly exhibited in these images. Additionally, a thin layer with the thickness of 1–2 nm between HfO₂ and Si substrate could be the SiO₂ film. As shown in Fig. 4a, there is no obvious lattice arrangement in the as-deposited HfO₂ film, indicating that this film is amorphous. After annealing at 400 °C, although most regions of HfO₂ film are still amorphous, we can observe that a fraction of lattice arrangements with the d-spacing values of 2.82 and 3.12 Å are formed in this film. These two d-spacing values are indexed to monoclinic HfO₂ (111) and monoclinic HfO₂ (−111) planes, respectively, and the 400 °C-annealed film shows the nanocrystalline structure. With increasing the annealing temperature from 400 to 600 °C, the crystal quality of HfO₂ film is gradually enhanced. When the HfO₂ film is annealed at 500–550 °C, the main lattice arrangements consisting of monoclinic HfO₂ (−111), monoclinic HfO₂ (200), and orthorhombic HfO₂ (111) can be identified. However, further increasing the annealing temperature to 600 °C, the lattice structure of orthorhombic HfO₂ (111) still exists in the film, and the other two lattice arrangements gradually disappear. On the other hand, the d-spacing values of orthorhombic HfO₂ (111) planes for the 500 °C-, 550 °C- and 600 °C-annealed HfO₂ films are determined to be 2.93, 2.90, and 2.88 Å, respectively. This agrees well with the XRD result that the orthorhombic HfO₂ (111) diffraction peak shifts towards to the high angle direction with increasing the annealing temperature from 500 to 600 °C. The result reveals that the oxygen content of HfO₂ film reduces gradually as the annealing temperature is increased. The other interesting phenomenon can be found in the changes of crystal structure and thickness of the SiO₂ layer. At the as-deposited state, the SiO₂ layer is amorphous. Even if the sample is annealed at 400 °C, the thermal energy is not high enough to transform the structure of SiO₂ layer from amorphous to crystalline. Nevertheless, by increasing the annealing temperature from 450 to 600 °C, the crystalline SiO₂ layer (with the cubic SiO₂ (220) structure) is formed and its thickness increases from 1.0 to 1.6 nm. It can be observed that the amorphous SiO₂ layer completely transforms to cubic SiO₂ structure after annealing the sample at 600 °C. With an increment of annealing temperature from 550 to 600 °C, the d-spacing value of cubic SiO₂ (220) increases from 2.48 to 2.56 Å. This means that the oxygen content of SiO₂ layer increases by increasing the annealing temperature. It can be reasonably speculated
that the addition of oxygen content in the SiO₂ layer is attributed to the diffusion of oxygen atoms sourced from the HfO₂ film. Moreover, the overall thickness decreases for the annealing temperature of 550 and 600 °C and might be related to the increase of the film density caused by crystallization and hydrogen removal.

Based on the above results, Fig. 5 illustrates the mechanisms of the HfO₂ films with different annealing temperatures. Considering the annealing temperature is smaller than 400 °C (Fig. 5a), the film is amorphous where Hf and O atoms are randomly arranged. The interfacial layer between HfO₂ and c-Si wafer is a mixed
oxide consisting of a-SiO₂ and a-HfO₂. At an annealing temperature of 450–550 °C (Fig. 5b), the HfO₂ film receives thermal energy leading to a structural change from amorphous to polycrystalline with monoclinic and orthorhombic phases. The crystalline orientation and d-spacing are indicated according to the HR-TEM and GIXRD results. A crystalline SiO₂ layer is formed. Several works reported an ordered silicon oxide layer at the interface of a-SiO₂ and (100) c-Si, but the mechanism and atomic-scale structure have remained controversial. Silicon thermal oxidation could be regarded as sequential inserting operations of oxygen atoms into Si-Si bonds, and this induces a large accumulation of compressive strains in the oxidized regions and might possibly cause a structural transformation into ordered oxide at the SiO₂/c-Si interface [24]. It has also been reported that crystalline oxygen-containing phase could be formed under conditions of high oxygen oversaturation of Si [25] or low interface defect density [26]. From the XPS and TEM images in this work, the HfO₂ layer is oxygen deficient. The significant amounts of oxygen diffuse from HfO₂ towards silicon substrate, and this might lead to oversaturation of oxygen at the c-Si interface and formation of crystalline SiO₂. In this temperature range, the crystalline SiO₂ layer thickness would increase but the a-HfO₂ + a-SiO₂ mixed layer thickness decreases with increasing annealing temperature. At an annealing temperature higher than 550 °C (Fig. 5c), the HfO₂ structure is dominated by polycrystalline orthorhombic (111) single phase. The interfacial layer is entirely governed by crystalline SiO₂. The d-spacing decreases for orthorhombic HfO₂ layer and increases for c-SiO₂. Although annealing of HfO₂ is necessary for achieving high Si wafer passivation and dielectric constant, at high temperatures,
Fig. 5 Diagrams of mechanism of crystallization of HfO$_2$ films and interfacial layer in the temperature ranges (a) as-deposited to 400 °C, (b) 450 to 550 °C, and (c) beyond 550 °C. The d-spacing value and crystalline orientation are also indicated.
the resultant crystallization of the HfO$_2$ and the interfacial SiO$_2$ may reduce the film properties. The annealing temperature of 500°C is found to obtain the best dielectric constant of 17.2. Further increasing the annealing temperature leads to a reduction in dielectric constant, possibly due to the change in the crystalline phase. Tomida et al. reported that the dielectric constant of HfO$_2$ decreases when the structure transformed from polycrystalline to monoclinic single phase [27]. The best passivation of HfO$_2$/Si can also be obtained at the annealing temperature of 500°C, as higher temperatures might lead to a complete c-SiO$_2$ interfacial layer and dehydrogenation at the interface.

**Conclusion**

HfO$_2$ films are prepared using RP-ALD, and effect of annealing temperature on crystalline structure of the HfO$_2$ has been investigated. For as-deposited HfO$_2$ and that annealed below 400 °C, the HfO$_2$ and the interfacial layer are amorphous. With increasing annealing temperature, the d-spacing of orthorhombic reduces while that of the c-SiO$_2$ interfacial layer increases, indicating the oxygen diffusion from HfO$_2$ to Si interface. Annealing temperature higher than 550 °C shows a HfO$_2$ layer with polycrystalline orthorhombic single-phase, and the interfacial layer completely transforms to c-SiO$_2$. Although annealing is required for HfO$_2$ in many applications such as achieving high passivation of Si wafers and high dielectric constant, the crystallization could be harmful to the film properties. The annealing temperature of 500 °C can have the best Si wafer passivation quality and dielectric constant.

**Abbreviations**

AFM: Atomic force microscopy; a-HfO$_2$: Amorphous hafnium oxide; ALD: Atomic layer deposition; a-SiO$_2$: Amorphous silicon dioxide; c-SiO$_2$: Crystalline silicon dioxide; GIXRD: Grazing incident X-ray diffraction; HfO$_2$: Hafnium oxide; HR-TEM: High-resolution transmission electron microscopy; N$_2$: Nitrogen; O$_2$: Oxygen; RMS: Root-mean-square; RP-ALD: Remote plasma atomic layer deposition; RTA: Rapid thermal annealing; TEMAH: Tetakis (ethylenediamino) hafnium; XPS: X-ray photoelectron spectroscopy

**Funding**

This work is sponsored by the Ministry of Science and Technology of Taiwan (nos. 104-2632-E-212-002-, 104-2622-E-212-005-CC3, 104-2221-E-212-002-MY3). This work is also sponsored by the National Natural Science Foundation of China (nos. 61534005 and 61474081), the Science and Technology Innovation Project of Xiamen (nos. 35022220183054 and 35022220173040), and the Science and Technology Program of the Educational Office of Fujian Province (UT180432).

**Availability of Data and Materials**

All data supporting the conclusions of this article are included within the article.

**Authors’ contributions**

XYZ carried out the characterization of the HfO$_2$ thin films and drafted the manuscript. CHH, WYW, SLO, and SYL led the experimental and analytical effort. SYC, WH, WZZ, FBX, and SZ contributed to the valuable discussion on experimental and theoretical results. All authors read and approved the final manuscript.

**Competing interests**

The authors declare that they have no competing interests.

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Received: 30 December 2018 Accepted: 25 February 2019
Published online: 07 March 2019

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