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Effects of rapid thermal annealing on interfacial and electrical properties of Gd-doped HfO_2 high-k gate dielectrics

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A B S T R A C T

In this work, we systematically investigated the effects of rapid thermal annealing on the interfacial and electrical properties, as well as band offsets of sputtering-derived Gd-doped HfO_2 film on Si substrate. The results indicate that annealing temperature has little effect on the interfacial properties of Gd-doped HfO_2 thin films, and the main component of interfacial layer is silicate without any silicide. Moreover, heat treatment can effectively improve the C–V characteristics of the samples, such as the increase of effective permittivity, reduction in ΔV_{fb} and no obvious frequency dispersion. However, the increase of annealing temperature leads to the increase of leakage current density of Al/Gd-doped HfO_2/Si MOS capacitor due to the decrease of the conduction band offset (ΔEc) and further crystallization of the samples. These investigation results might provide the guidance for the performance optimization of high k gated dielectrics to meet the requirements of future complementary-metal-oxide-semiconductor (CMOS) devices.

1. Introduction

Hf-based oxides such as HfON [1,2], HfAlO [3], HfTiON [4–6], HfLaON [7], HfSiO [8,9] and HfSiON [10] have been extensively studied as the promising alternatives to conventional gate oxide SiO_2 in ultrascaled CMOS devices due to its relative wide band gap and good thermal stability on silicon which can effectively reduce the tunneling leakage current of CMOS applications. Moreover, the recent studies indicate that rare earth (RE) oxides incorporated into HfO_2 gate dielectric can effectively increase permittivity, change the electronic structure, suppress the formation of oxygen vacancies, and enlarge band gap and conduction band offset, thus improving the properties of Hf-based oxides for application in CMOS [11–16].

Meanwhile, it is well known that heat treatment is an important process to optimize the properties of the high-k gate dielectric for high performance CMOS transistor. Researches have been focused on the properties of Gd-doped HfO_2 films with and without RTA [17], however, the changes of the interfacial and electrical properties related with annealing temperature have not been systematically investigated. Herein, we demonstrated the evolution of the interfacial and electrical properties of Gd-doped HfO_2/Si gate stack as a function of annealing temperature in detail. In addition, the band gaps as well as the band offsets of Gd-doped HfO_2 films have also been systematically investigated.

2. Experimental

The Gd-doped HfO_2 thin films were prepared on n-type Si (100) wafers with a resistivity of 1–10 Ω cm and quartz substrates by radio frequency (RF) reactive sputtering using HfGdO (atomic ratio of Hf:Gd = 9:1) ceramic target. Prior to deposition, the Si substrates were cleaned by a modified RCA method followed by diluted HF solution etching to remove native oxide on the surface, then the substrates were dried with N_2 atmosphere. The working pressure, deposition power, and deposition temperature were fixed at 0.5 Pa, 60 W and room temperature, respectively. Ex situ rapid thermal

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annealing (RTA) was conducted under high vacuum ambient condition (8.5×10^{-5} mbar) at the temperature of 300, 500, and 700 °C, respectively. Nearly 50 nm thick Gd-doped HfO_2 film was deposited on n-Si (100) substrate for X-ray diffraction (XRD) analysis. About 5 nm thick Gd-doped HfO_2 film was obtained for X-ray photoelectron spectroscopy (XPS) analysis to investigate the film composition and chemical bonding state. The XPS measurements were carried out by an ESCALAB 250Xi system, equipped with an Al Kα radiation source (1487.6 eV) and all the collected data were corrected using the binding energy of C1s peak (284.8 eV) [18]. Approximately 50 nm thick Gd-doped HfO_2 film were deposited on quartz substrate to test their optical band gap by ultraviolet–visible (UV–Vis) transmission spectroscopy. In order to fabricate MOS capacitors, about 14 nm Gd-doped HfO_2 films were deposited on n-Si substrate. Al circle pads with diameter of 300 μm were deposited as metal gate electrodes by DC sputtering. The thickness of Gd-doped HfO_2 films were determined by spectroscopy ellipsometry.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-deposited and annealed Gd-doped HfO_2 samples at different annealing temperatures. For the as-deposited sample, the weak diffraction peaks attributed to monoclinic structure of HfO_2 has been detected, indicating the as-deposited film has been crystallized. After annealing at 300 °C, no obvious change can be observed from the XRD pattern, demonstrating that the film remains monoclinic structure. With the increase of the annealing temperature to 500 °C, the widths of characteristic peaks become broad indicating new peaks emerge. When annealing temperature reaches to 700 °C, the new peaks corresponding to tetragonal structure of HfO_2 can be observed, revealing that Gd-doping leads to stabilize high temperature tetragonal structure of HfO_2 to room temperature.

In order to investigate the interfacial chemical states of Gd-doped HfO_2 thin films, the profiles of Hf 4f, Gd 4d, O 1s, and Si 2p chemical states were examined using XPS. The observed chemical ratio of the HfGdO film is $HfGd_{0.14}O_{4.75}$, $HfGd_{0.11}O_{4.43}$, $HfGd_{0.14}O_{4.68}$, and $HfGd_{0.14}O_{5.04}$ of as-deposited, annealed at 300, 500 and 700 °C, respectively. The results indicate that the changes in Hf and Gd composition in the samples are consistent with that of in the targets.

Annealing temperature dependent Hf 4f core-level spectra of Gd-doped HfO_2 thin films are shown in Fig. 2. For all the samples, Hf 4f peak could be deconvoluted into two peaks by a standard Gaussian curve-fitting procedure, originating from the Hf $4f_{7/2}$ and Hf $4f_{5/2}$ bonding states, which can be fitted by a spin orbit doublet with an energy splitting of about 1.6 eV [19]. For the as-deposited sample, Hf 4f double peaks locate at 16.55 and 18.18 eV, respectively. With the annealing temperature increases from 300 to 700 °C, the corresponding binding energies of Hf 4f peaks shift towards the direction of the higher energy, indicating the formation of Hf-silicate($HfSiO_x$) during annealing [20]. There is no peak located at lower binding energy, indicating no deleterious Hf/Gd–Si bond is formed, regardless of annealing temperature [20].

Fig. 3 presents O 1s core level spectra of the as-deposited and subsequently annealed Gd-doped HfO_2/Si system at 300, 500 and 700 °C, respectively. O 1s peak of all the samples could be deconvoluted into two peaks with only slight difference in the binding energy, located at about 529.6 and 531.3 eV, corresponding to O–Hf(Gd) and silicate [6], respectively, indicating the film consist of a nonstoichiometric O–Hf(Gd) and silicate interfacial layer [21].

The Si 2p XPS spectra of as-deposited and annealed samples are demonstrated shown in Fig. 4. It can be seen that except Si–Si bond appears at about 98.8 eV for all the samples, another peak located at about 102.7 eV corresponding to silicate is found [22]. No peak located at 103.7 eV originating form O–Si bonds in SiO_2 is observed indicating no SiO_2 interfacial layer is formed between the samples and Si substrate [2]. Combining to O1s XPS spectra, it is concluded

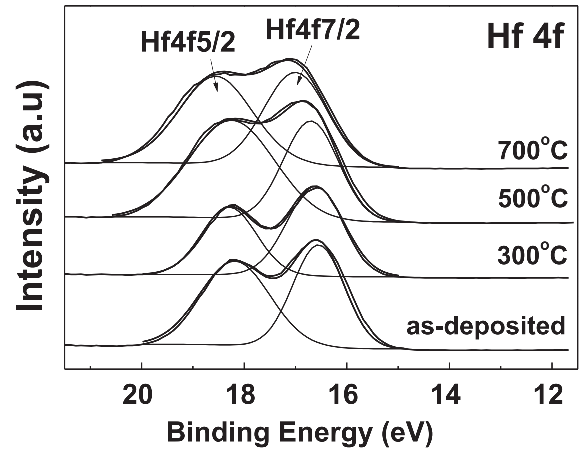

Fig. 2. Hf 4f XPS spectra of Gd-doped HfO_2 thin films at different annealing temperature.

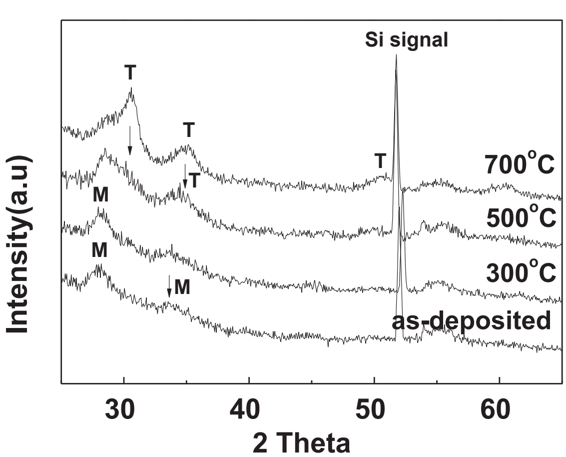

Fig. 1. XRD patterns of Gd-doped HfO_2 thin films deposited at different annealing temperature.

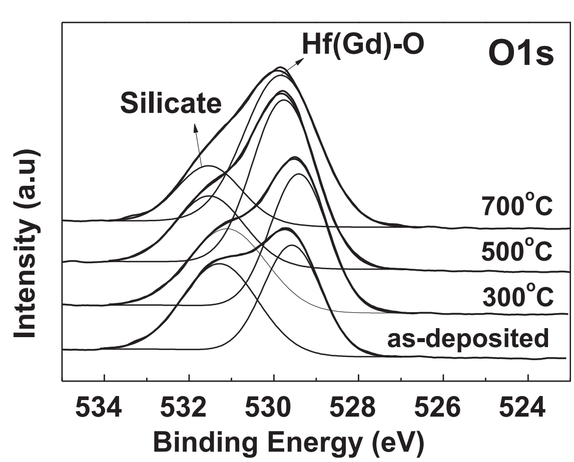

Fig. 3. O 1s XPS spectra of Gd-doped HfO_2 thin films at different annealing temperature.