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Microstructure optimization and optical and interfacial properties modulation of sputtering-derived HfO_2 thin films by TiO_2 incorporation

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ABSTRACT

TiO_2-doped HfO_2 gate dielectric thin films have been deposited on Si(100) substrates by RF sputtering. The component, morphology, structure, optical and interfacial properties of $Hf_{1-x}Ti_xO_2$ films related to TiO_2 concentration are systematically investigated by atomic force microscope (AFM), X-ray diffraction (XRD), spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), and Fourier transformation infrared (FTIR). By employing Cauchy–Urbach model, the optical constants, such as refractive index (n), extinction coefficient (k), absorption coefficient (α), and optical band gap (E_g) have been determined precisely. Measurements from XRD have confirmed that TiO_2 incorporating into HfO_2 films leads to the increase of the crystallization temperature of HfO_2 films with increasing the TiO_2 concentration. SE analyses have indicated that reduction in band gap and refractive index has been observed with increasing the TiO_2 component in $Hf_{1-x}Ti_xO_2$ films. The increase in Urbach parameter E_U with the increase of TiO_2 concentration also suggests the rise in disorder for $Hf_{1-x}Ti_xO_2$ films. FTIR measurements for $Hf_{1-x}Ti_xO_2$/Si gate stack indicate the existence of the interfacial layer regardless of the TiO_2 concentration. For the 9% TiO_2-doped HfO_2 samples, the shift in FTIR characteristic peak suggests the formation of the silicate layer, which leads to the suppressed interfacial layer growth during deposition. As a result, it can be conclude that the TiO_2 component in $Hf_{1-x}Ti_xO_2$ films should be controlled precisely to guarantee interfacial properties of $Hf_{1-x}Ti_xO_2$/Si gate stacks.

1. Introduction

According to the International Technology Roadmap for Semiconductors (ITRS), an equivalent oxide thickness of less than 1.0 nm is required to meet the requirements for MOSFET devices [1]. As scaling becomes less effective in state-of-the-art conventional CMOS technologies for nanoscale nodes, high-k materials have been extensively investigated for the application of 45 nm generation and beyond. Large gate capacitance can be obtained even for thicker films on the account of large k value, and so direct tunneling of carriers can be effectively suppressed [2–4]. Among these high-k candidates, HfO_2 high-k gate dielectric has attracted much attention due to its relatively high dielectric constant, wide band gap, and good stability with Si [5]. However, pure HfO_2 film has low crystallization temperature, which would result in a thick low-k interfacial layer, instable threshold voltage, defect generation, and high leakage current densities. In order to improve its crystallization temperature and electrical properties, some elements were incorporated into HfO_2 film, such as Al [6], or Ta [7] to form HfO_2-based gate dielectrics, which have been reported to be suitable for MOSFET devices with excellent reliability and high performance. Recently, it has been reported that $Hf_{1-x}Ti_xO_2$ has been regarded as the most promising high-k gate dielectrics due to its considerably sufficient energy band gap, high dielectric constant, and compatibility with (CMOS) processes [8,9]. As known, TiO_2 is a high-k material possessing k value of about 80 due to a strong contribution from soft phonons [10,11]. What is more, Ti and Hf are both 4-valence elements, much less oxygen vacancy will exist in $Hf_{1-x}Ti_xO_2$ thin film, which will reduce leakage current in CMOS device based on $Hf_{1-x}Ti_xO_2$ high-k gate dielectric. Although the improved electrical performance for

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TiO_2-doped HfO_2 gate dielectrics [9,12,13], the detailed investigation on the evolution of the microstructure and optical properties of $Hf_{1-x}Ti_xO_2$ as a function of TiO_2 concentration have not been systematically investigated. The precise determination of optical constant and microstructure modulation of $Hf_{1-x}Ti_xO_2$ film related to TiO_2 incorporation component will play an important role for $Hf_{1-x}Ti_xO_2$ application as potential high-k candidates in CMOS devices. Meanwhile, the addition of TiO_2 into HfO_2 would lead to the decrease of crystallization temperature of HfO_2 and the formation of low-k interfacial layer due to interface reaction, and thus deteriorate the interface quality and also increase the leakage current [10]. Therefore, TiO_2 concentration of $Hf_{1-x}Ti_xO_2$ gate dielectric requires to be carefully controlled to yield the optimal values which satisfy the demands of high-k gate dielectrics in CMOS devices. In current work, microstructure optimization and optical properties modulation of HfO_2 thin films by TiO_2 incorporation have been investigated. Current work will help to fill this gap by reporting the structural and optical properties of $Hf_{1-x}Ti_xO_2$ films, and their dependence on the TiO_2 concentration. As a well-developed film technique, sputtering has many advantages such as simple apparatus, low deposition temperature, high deposition rate, good adhesion and uniformity and suitability for large area deposition [14]. In this letter, we reported the effect of the TiO_2 concentration on the compositional, structural and optical characteristics of sputtering-derived $Hf_{1-x}Ti_xO_2$ films on Si substrate. The correlation between structural characteristics and optical and morphological properties was systematically studied with X-ray diffraction (XRD), atomic force microscopy (AFM), variable angle spectroscopy ellipsometry (SE). FTIR measurement provides the information on the evolution of the interfacial layer of $Hf_{1-x}Ti_xO_2$/Si gate stack as a function of TiO_2 incorporation component.

2. Experimental details

Before deposition, p-type Si(1 0 0) substrates with a resistivity of 2–5 Ω cm were ultrasonically cleaned in acetone and ethanol for 10 min to remove any impurity element. Then, silicon wafers were dipped in 1% buffered HF solution to remove any native oxide on the surface and other impurity ions that had adhered to the surfaces of the wafers. Finally, the substrates were dried by N_2 gun and put into the deposition chamber. Prior to the $Hf_xTi_{1-x}O_2$ film deposition, the sputtering chamber was initially pumped down to a base pressure of 3.0×10^{-4} Pa to remove residual oxygen to prevent the oxidation of the silicon surface. Ar gas with purity of 99.999% was introduced into the chamber by separate inlets and controlled by standard mass flow controllers. To remove the surface contaminants on the target and stabilize the sputtering, the $Hf_xTi_{1-x}O_2$ target is pre-sputtered for 10 min. The $Hf_xTi_{1-x}O_2$ thin films were grown on Si substrate from $Hf_xTi_{1-x}O_2$ target with a diameter of 60 mm (TiO_2 content in the composite target was fixed at 1%, 3%, 5%, and 9%). The deposition conditions are listed in Table 1. Post-deposition anneal (PDA) for all samples was performed at 600 °C for 30 min in air. All the as-processed samples with different TiO_2 incorporation component were denoted as S1, S2, S3 and S4, respectively. Film microstructure was analyzed by X-ray diffraction (XRD, MXP 18AHF MAC Science, Yokohama, Japan). The X-ray source was Cu Kα, with an accelerating voltage of 40 kV, a current of 100 mA, scanning range from 20° to 80°, glancing angle of 2°, scanning step of 0.02°, and scanning speed of 8°/min. The surface morphology was investigated by using atomic force microscopy (AFM). The film roughness was demonstrated by the root mean square value (RMS) in 2 μm × 2 μm area. FTIR measurements in the spectral range 400–1200 cm^{-1} were carried out using a Thermo Nicolet MagnaIR 760 spectrophotometer equipped with a deuterated triglycine sulfate detector with KBr windows and an XT-KBr beam splitter, whose measurements resolution was 8 cm^{-1}. Optical properties measurements were carried out by a spectroscopic ellipsometry (SC630, SANCO Co, Shanghai) over a spectrum range of 190–900 nm where Cauchy–Urbach model was used to obtain the optical constants. The thicknesses and optical constants of the $Hf_xTi_{1-x}O_2$ films with different TiO_2 concentration were obtained by analyzing the measured ellipsometric spectra through the Cauchy–Urbach model. *Ex situ* XPS measurements for $Hf_{1-x}Ti_xO_2$ were performed to confirm the component of the $Hf_xTi_{1-x}O_2$ films by using (ESCALAB 250Xi) system, equipped with an Al Kα radiation source (1487.6 eV) and hemispherical analyzer with a pass energy of 20 eV. The collected data were corrected for charging effect-induced peak shifts using the binding energy (BE) of C 1*s* peak (285.15 eV).

Table 1
Sputtering parameters for $Hf_{1-x}Ti_xO_2$ films.

Base pressure (Pa)	3.5×10^{-4}
Working pressure (Pa)	0.25
Ar gas flow (SCCM)	20 SCCM
Sputtering power (W)	60 W
Substrate temperature (°C)	Room temperature
Substrate-target distance (mm)	60 mm

3. Results and discussion

3.1. Structural properties

XRD characterization was carried out to investigate the evolution of the microstructure of $Hf_{1-x}Ti_xO_2$ films as a function of TiO_2 concentration, as shown in Fig. 1. For the $Hf_{1-x}Ti_xO_2$ films with TiO_2 concentration less than 3%, it can be noted that several diffraction peaks located at around 28°, 34° and 50° of 2θ corresponding to the (−1 1 1), (0 0 2) and (2 2 0) monoclinic phase of HfO_2 have been observed [15,16]. Meanwhile, a preferential orientation along the (−1 1 1) direction has been detected for these samples. At the same time, the crystallization quality of $Hf_{1-x}Ti_xO_2$ films becomes poor with the increase in TiO_2 concentration. When the doping concentration for TiO_2 in $Hf_{1-x}Ti_xO_2$ films arrives to 9%, all the diffraction peaks attributed to the monoclinic phase of HfO_2 disappear and the film shows an analogously amorphous structure. According to previous publication, it can be noted that poor crystallinity in the TiO_2-doped HfO_2 films has been observed, which can be due to the fact that the TiO_2 incorporation in film network enables more nucleation sites which, in turn, inhibit the growth of crystal grains. Assuming homogeneous strains across crystallites, the mean grain size is esteemed from the (−1 1 1) peak width using the Debye–Scherrer's formula [17]:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where λ, θ and β are the X-ray wavelength (1.54056 Å), Bragg diffraction angle, and line width at half maximum of the most dominant peak, respectively. Meanwhile, the lattice strain (ε) of the as-deposited films has been determined using the tangent formula:

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{2}$$

where θ is the (−1 1 1) diffraction angle. The calculated grain sizes and lattice strain with different TiO_2 doping concentration are shown in Table 2. It can be seen that the grain size decreases with the increase in TiO_2 concentration. The broadening in peak with increasing TiO_2 concentration is also observed, suggesting that the HfO_2 crystalline quality is deteriorated by TiO_2 incorporation.

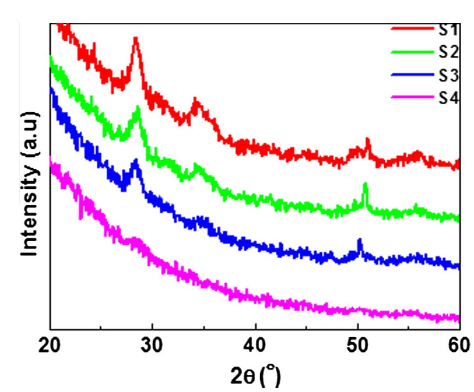

Fig. 1. XRD spectra of the TiO_2-doped HfO_2 thin films.