Applied Surface Science 384 (2016) 376–379

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effects of oxygen partial pressure and annealing temperature on the residual stress of hafnium oxide thin-films on silicon using synchrotron-based grazing incidence X-ray diffraction

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ARTICLE INFO

Article history:
Received 2 February 2016
Received in revised form 3 May 2016
Accepted 3 May 2016
Available online 18 May 2016

Keywords:
High-κ dielectric
Hafnium oxide
Crystallization
Residual stress

ABSTRACT

Synchrotron radiation-based grazing incidence X-ray diffraction (GI-XRD) technique is employed here to estimate the residual stress of < 10 nm thin hafnium oxide film deposited on Si (100) substrate at different argon/oxygen ratios using reactive rf sputtering. A decrease in residual stress, tensile in nature, is observed at higher annealing temperature for the samples deposited with increasing argon ratio in the Ar/O_2 plasma. The residual stress of the films deposited at higher p_{Ar} ($Ar:O_2 = 4:1$) is also found to be decreased with increasing annealing temperature. But the stress is more or less constant with annealing temperature for the films deposited at lower Ar/O_2 (1:4) ratio. All the above phenomena can be explained on the basis of swelling of the interfacial layer and enhanced structural relaxation in the presence of excess Hf in hafnium oxide film during deposition.

1. Introduction

Research on different metal oxides has been going on to get high-κ-based gate dielectric materials that can effectively replace SiO_2, the conventional gate oxide, due to the requirement of the semiconductor industry. Among the materials, HfO_2 has consolidated its position to act as an alternative to the SiO_2 gate dielectric due to its better thermal and chemical stabilities with Si, higher band gap ($\geq$ 5 eV) and larger conduction band offset. Reduction of the gate leakage current through the HfO_2 has still been a challenge [1–10]. Recently published results show that the crystallization of hafnium oxide film improves the leakage current characteristics of the metal-oxide-semiconductor (MOS) devices and mechanical stress is considered there as the root cause of the hafnium oxide crystallization [11]. Studies on the mechanical properties of thin hafnium oxide or similar high-κ metal oxide films are of great importance because of their elastochemical response on the thermal cycles experienced by the oxides during the device fabrication process [12]. Such responses also affect the electrical properties of the MOS-based devices. Attempts have been made by various researchers to measure the residual stress of thicker films by different methods [12–15]. But no information is so far available on the measurement of residual stress of < 10 nm-thick hafnium oxide films grown/deposited on Si substrate. The role of Si substrate and interfacial layer on the residual stress of high-κ dielectric film, grown/deposited on Si, was not also studied earlier. In this article, residual stress estimation of the thin hafnium oxide film on Si, deposited by reactive sputtering under different Ar/O_2 ratios and annealing conditions is made using synchrotron radiation-based GI-XRD measurements.

2. Experimental

Hafnium oxide films were deposited at room temperature (25 °C) on *n*-type Si (100) substrate of resistivity of 0.1–0.5 Ω cm by reactive rf magnetron sputtering using 99.9% pure Hf metal target. After attaining a base pressure of 3.4×10^{-6} mT, the deposition pressure was maintained at 5 mT by a programmable throttle valve. Depositions were carried out for 7.5 min with rf power of 50 W at oxygen partial pressures of 1, 2, 3 and 4 mT. Before loading into the sputtering chamber for deposition, all Si substrates were cleaned by the RCA technique followed by a 1-min dip in 1% hydrofluoric acid to remove the organic, metal contaminates and native oxide layer from Si surface, respectively [16,17]. The deposited samples were then subjected to rapid thermal annealing at 575, 650 and 1100 °C in N_2 environment. The deposition and annealing conditions of the

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http://dx.doi.org/10.1016/j.apsusc.2016.05.015
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Table 1
Deposition and annealing conditions of the samples.

Sample name	Annealing temperature (°C)	Ar:O_2
A650	650	1:4
A1100	1100	1:4
B1100	1100	2:3
C1100	1100	3:2
D1100	1100	4:1
D650	650	4:1
D575	575	4:1

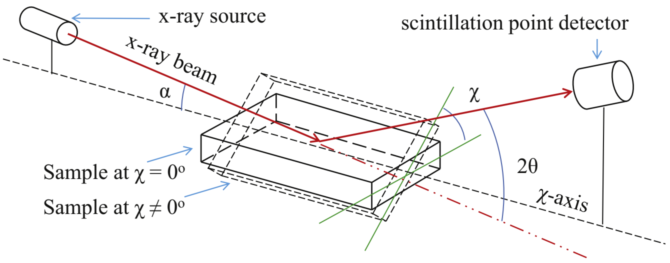


Fig. 1. A schematic diagram of GI-XRD setup for stress measurement.

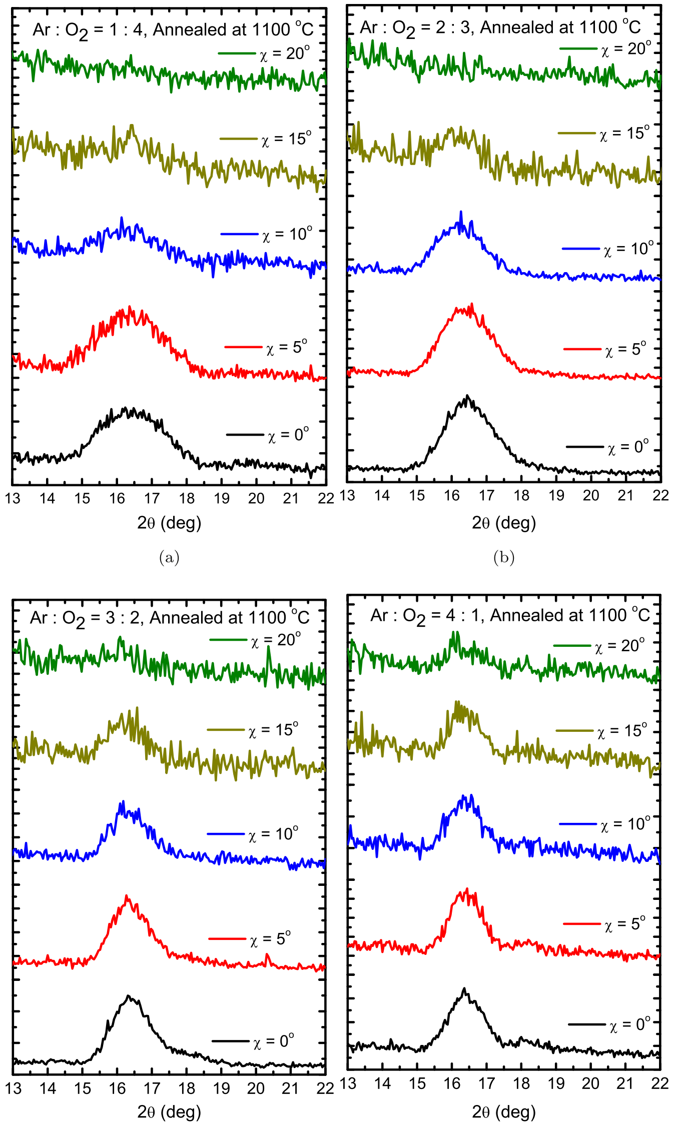
samples are summarized in Table 1. The stress measurements on all the samples were performed by the GI-XRD at BL-12 beam line at Indus – 2 synchrotron source with a wavelength of 0.8996 Åusing a six circle diffractometer (Huber 5020) with a scintillation point detector. A schematic diagram of the experimental setup is shown in Fig. 1. The grazing angle (α) was fixed at 0.3°. The wavelength was calibrated using X-ray diffraction pattern from the NIST (National Institute of Standards and Technology) of Si standard. Fig. 1 shows the diffraction of a monochromatic X-ray beam at an angle (2θ) from the surface of the sample for different substrate orientations. The χ is the angle between the normal to the sample surface and the incident and diffracted beam bisector which defines the orientation of the sample surface. The residual stress was estimated from the shift of the diffraction angle (2θ) due to the change in the lattice spacing at different χ orientations [18–24]. Generally, higher diffraction angle (2θ) is selected during stress measurements for better accuracy. But the presence of diffraction peak of Si substrate at ~ 31° and the polycrystalline and textured nature of the film, the m-HfO_2 with ($\bar{1}11$) plane at 16.434° is considered here for stress estimation of the samples, deposited and annealed under different conditions [19,20,25]. A 2θ scan was performed in the range of 13–22°. The χ angle was then varied by 5, 10, 15 and 20° and 2θ scan for each χ rotation was, respectively performed. The diffraction peak disappears for a χ value beyond 20° probably due to a strong degree of textured nature of the film. The GI-XRD measurements were carried out on the all samples using the above technique.

3. Results and discussions

Fig. 2, a representative GI-XRD data, shows the diffraction peaks of hafnium oxide, deposited on Si at different oxygen partial pressures and annealed at 1100 °C, at different χ positions. The centre of the Bragg peak for each χ-orientation are identified with the Gaussian curve-fitting method [20] and are used for the estimation of the residual stress. The expression for residual stress (σ) may be written as [18],

$$\sigma = -\frac{E}{2(1+\nu)}\frac{\pi}{180}\cot\theta_0\frac{\partial(2\theta)}{\partial\sin^2\chi} \tag{1}$$

where E and ν are Young's modulus and Poisson's ratio of the thin-film, respectively. The diffraction peak for a bulk stress free HfO_2 at the wavelength of 0.8996Å is found to be at 16.434 ° which



(a) (b)

(c) (d)

Fig. 2. GI-XRD measurements of the hafnium oxide films deposited at various Ar:O_2 ratios and annealed at 1100 °C for different χ values [Ar:O_2 – (a) 1:4 (b) 2:3 (c) 3:2 and (d) 4:1].

is considered here as θ_0 [25]. The values of the elastic constants and Poisson's ratio for the HfO_2 film are available in the literature [12,25–29]. Further, the relation between q_z, the wave vector along the Z direction and, θ can be expressed as

$$q_z = \frac{4\pi\sin\theta}{\lambda} \tag{2}$$

Therefore,

$$2\theta = \sin^{-1}\left(\frac{q_z}{4\pi}\right)$$

Hence,

$$\partial(2\theta) = \frac{2\lambda}{4\pi\sqrt{\left[1-\left(\frac{q_z\lambda}{4\pi}\right)^2\right]}}\partial q_z \tag{3}$$