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Optical and electrical properties of plasma-oxidation derived HfO_2 gate dielectric films

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Abstract

High-*k* gate dielectric HfO_2 thin films have been deposited on Si(1 0 0) by using plasma oxidation of sputtered metallic Hf thin films. The optical and electrical properties in relation to postdeposition annealing temperatures are investigated by spectroscopic ellipsometry (SE) and capacitance–voltage (*C–V*) characteristics in detail. X-ray diffraction (XRD) measurement shows that the as-deposited HfO_2 films are basically amorphous. Based on a parameterized Tauc–Lorentz dispersion mode, excellent agreement has been found between the experimental and the simulated spectra, and the optical constants of the as-deposited and annealed films related to the annealing temperature are systematically extracted. Increases in the refractive index *n* and extinction coefficient *k*, with increasing annealing temperature are observed due to the formation of more closely packed thin films and the enhancement of scattering effect in the targeted HfO_2 film. Change of the complex dielectric function and reduction of optical band gap with an increase in annealing temperature are discussed. The extracted direct band gap related to the structure varies from 5.77, 5.65, and 5.56 eV for the as-deposited and annealed thin films at 700 and 800 °C, respectively. It has been found from the *C–V* measurement the decrease of accumulation capacitance values upon annealing, which can be contributed to the growth of the interfacial layer with lower dielectric constant upon postannealing. The flat-band voltage shifts negatively due to positive charge generated during postannealing.
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Keywords: High-*k* gate dielectrics; HfO_2 thin films; Plasma oxidation; Optical properties; Interfacial layer

1. Introduction

The aggressive scaling of CMOS devices is driving SiO_2-based gate dielectric to its physical limits, as stated in the international roadmap for semiconductors (ITRS) [1]. As an alternative to continuing to scale SiO_2, recent effort has focused on the development of alternative high-*k* gate dielectrics with physical and electrical properties suitable for integration with standard CMOS technology [2–8]. Unfortunately, many high-*k* candidates have been found to be thermally unstable with silicon, with a resultant low permittivity interfacial layer forming between the silicon and the high-*k* films. Among the high-*k* dielectrics being studied, HfO_2 has proven to be one of the most promising candidates due to its reasonably high dielectric constant (~25), a relatively large band gap (5.68 eV) [9], high heat of formation (271 kcal/mol) and good thermodynamic stability when in direct contact with Si. Despite their potential dielectric and optoelectronic applications, the optical properties of HfO_2 thin films have not been thoroughly investigated. Since accurate determination of the optical functions is essential prerequisites for device simulations and gives the opportunity to improve material preparation, this necessitates the investigation of optical characteristics for HfO_2 thin films in the wide energy range.

Many deposition techniques for gate dielectric have been explored such as physical vapor deposition [10,11], chemical vapor deposition [12] and atomic layer deposition [13]. Among these deposition techniques, one of the serious problems is the interfacial layer growth due to the oxidization of the Si substrate surface, which is brought about in excess oxygen ambient at elevated temperature .In addition, the existence of residual impurities in the deposited film by ALD due to the use

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of precursor is unfavorable to the quality of HfO_2 gate oxide [14]. Lysaght et al. have reported the void formation in the film by the etching effect of Cl impurity containing in the reaction precursor [15]. These technical problems in the ALCVD technique are related to lessen MOS device reliability.

Compared with the deposition methods, PVD-based methods have been pursued to prepare high-*k* films due to its simpleness and lower contaminants [16]. Additionally, besides the advantages mentioned above, PVD has shown easily controllable growth of low-*k* interfacial layer at low temperature process and compositional consistency between the target and the deposited film. Meanwhile, plasma oxidation offers a low temperature processing and blocks the diffusion of oxygen content from the ambient, which prevent the reaction of interfacial layer. PVD combined with plasma oxidation of sputtered metallic films will have the possibility in obtaining the high-quality high-*k* gate dielectric thin films. Therefore, in this paper, we report on a plasma oxidation of sputtered metallic hafnium films to form the stoichiometric HfO_2 at temperature as low as 400 °C and focus on the effect of the postdeposition annealing on the optical and electrical properties of the targeted films on silicon substrate.

2. Experimental

2.1. Preparation of HfO_2 films

Before deposition, *p*-type Si(1 0 0) substrates with a resistivity of 2–5 Ωcm were cleaned by a modified RCA process and dipped in 1% buffered HF solution to remove any native oxide and to hydrogen passivate the surface. After the chemical treatment process, the substrates were dried and put into the deposition chamber with a cylindrical stainless-steel chamber connected to a turbomolecular pump. The sputtering target was a Hf disk of 99.99% purity with the diameter of 60 mm. The chamber was initially evacuated to 8.5×10^{-5} Pa, and ultra-high purity (99.999%) Ar was introduced to act as the sputtering enhancing gas. Prior to Hf deposition, the hafnium metal target was pre-sputtered in an argon atmosphere for 10 min in order to remove surface oxide of the target, and then a hafnium metal layer was pre-deposited by a direct current magnetron sputtering in Ar ambient at room temperature. The sputtering power density for hafnium was 3 W/cm^2 and the sputtering target used in this experiment was a high-pure hafnium metal (99.99%). After the Hf metal layer deposition, the wafers were ex situ transferred to plasma oxidation chamber and the as-deposited Hf metal layer was oxidized by Ar/O_2 plasma generated in the chamber. The plasma was inductively coupled plasma with an RF power of 2 kW, a frequency of 13.56 kHz. During oxidation, the flow rate of Ar and the O_2 flow rate were held at 30 and 5 sccm, respectively; the reactor chamber pressure was kept at 15 Pa and the Si substrates. According to our previous report, HfO_2 thin films has a low crystallization temperature of 500 °C [17]. In order to keep the targeted thin films amorphous state, the plasma oxidation of sputtered Hf metal layer proceeded at 400 °C. The time of plasma oxidation was 2 min. If the time is shortened, the sputtered metallic Hf films will not oxidize fully; If the time is lengthened, the oxygen from the ambient will diffuse into the interface and leads to the acceleration of the reaction of the interface layer, which is not expected in our experiment. In order to improve the qualities of the resultant HfO_2 films, additional post oxidation annealing was performed at 500–900 °C for 5 min in N_2 ambient.

2.2. Film characterization

Spectroscopic ellipsometry (SE) measurement from 0.75 to 6.5 eV in 0.05 eV step were carried out in a spectroscopic phase modulated ellipsometer (Model UVISEL JOBIN-YVON) at room temperature. SE determines the ratio of diagonal reflection Jones matrix elements $r_{pp}/r_{ss} = \tan \Psi \exp^{i\Delta}$, where $r_{pp}(r_{ss})$ is the complex Fresnel reflection coefficient parallel (perpendicular) to the plane of incidence, respectively. Ψ and Δ are the ellipsometric angles reported as $\tan \Psi$ and $\cos \Delta$. According to the ellipsometric data Ψ and Δ, the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ can be determined. In our SE data analysis, the unknown dielectric function of HfO_2 is described by the TL model developed by Jellison and Modine [18,19] as expressed in the following:

$$\varepsilon_2(E) = \frac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2+C^2E^2}\frac{1}{E} \qquad (E > E_g) \tag{1}$$

$$\varepsilon_2(E) = 0 \qquad (E \le E_g) \tag{2}$$

$$\varepsilon_1(E) = \varepsilon_\infty + \frac{2P}{\pi}\oint \frac{\xi\varepsilon_2(\xi)}{\xi^2-E^2}\mathrm{d}\xi \tag{3}$$

Above equations as functions of the photon energy E are uniquely defined by five parameters A (transition matrix element, related to the film density [20]), E_0 (peak transition energy, corresponds to the Penn gap which represents an average separation between valence and conduction bands [21]), C (broadening term, which can be related to the degree of disorder in the material [20]), E_g (optical band gap), and ε_∞ (high frequency dielectric constant). Thus, using the TL model, the dispersion of the optical constants can be described by the five parameters A, C, E_0, E_g and ε_∞, respectively. The mode structures and optical properties of the films were optimized by least-squares refinements (χ^2) defined as the figure of merit of the fitted function. For interpreting the measured pseudodielectric function, a four-layer-structured optical model consisting of a Si(1 0 0) substrates (the optical constant taken from SE measurement on an reference *c*-Si film [22]), the SiO_2 interface layer contributed to the diffusion of oxygen and reaction with Si substrate from the sputtering ambient (the optical constant taken from Ref. 23), a bottom bulk HfO_2 layer, and a surface rough layer composed of 50% void space and 50% HfO_2, modeled by an effective medium approximation applying the Bruggeman formalism [24], has been constructed for each sample to determine the optical properties of the as-deposited and annealed HfO_2 films. Variables in the fitting procedure included the layer thickness and the dispersion relation describing the optical properties of the HfO_2 itself.

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