Materials Science in Semiconductor Processing 29 (2015) 321–325

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Structural, optical and dielectric properties of HfSiO films prepared by co-evaporation method

Chen Yang*, Lingxia Hang, Junqi Xu

Shaanxi Province Thin Film Technology and Optical Test Open Key Laboratory, Xi'an Technological University, Xi'an, 710032, China

ARTICLE INFO

Available online 5 June 2014

Keywords:
HfSiO dielectric film
Co-evaporation
Optical and electrical properties

ABSTRACT

HfSiO dielectric films were prepared on Si substrate by the co-evaporation method. The chemical composition, crystalline temperature, optical and electrical properties of the compound film were investigated. X-ray photoelectron spectroscopy analysis illustrated that the atom ratio of Hf to Si was about 4:1 and Hf–Si–O bonds appeared in the film. The X-ray diffraction analysis revealed that the crystalline temperature of the film was higher than 850 °C. Optical measurements showed that the refractive index was 1.82 at 550 nm wavelengths and the optical band gap was about 5.88 eV. Electrical measurements demonstrated that the dielectric constant and a fixed charge density were 18.1 and 1.95×10^{12} cm^{-2} respectively. In addition, an improved leakage current of 7.81 μA/cm^2 at the gate bias of −3 V was achieved for the annealed HfSiO film.

1. Introduction

Silicon dioxide has been used as a gate oxide material for decades. As transistors have decreased in size, the thickness of the silicon dioxide gate dielectric has steadily decreased to increase the gate capacitance and thereby drive current and device performance. As the thickness scales below 2 nm, leakage currents due to tunneling increase drastically, leading to unwieldy power consumption and reduced device reliability. However, it has been found that replacing the silicon dioxide gate dielectric with a high-k material could increase gate capacitance without the concomitant leakage effects [1,2].

Usually, rare earth oxides with a high relative dielectric constant ($k \geq 20$), such as TiO_2, ZrO_2, Pr_2O_3,Yb_2O_3, Gb_2O_3, La_2O_3 and HfO_2, are currently being investigated as potential replacements for SiO_2 in the next generations of complementary metal-oxide-semiconductor (CMOS) devices [3–8]. Among the referred candidates, HfO_2 has been regarded as the most prospective one to replace silicon dioxide not only because of its high permittivity ($k \approx 25$), but also because of its larger band gap (5.5 eV) and thermal stability when deposited on silicon substrates [9]. However, it is difficult to integrate it directly into the existing CMOS process owing to its shortcoming of a low crystallization temperature of 600 °C. As known, crystallization will induce high leakage current and severe mass transport along the grain boundaries resulting in a degrading device performance. It is reported that incorporation of Si element into HfO_2 can improve its thermal stability and the formed new high-k gate dielectrics Hf_xSi_yO have quite improved electronic characteristics and met the requirements of the future advanced CMOS device. Therefore, Hf_xSi_yO film has been extensively studied recently. Moreover, the silicate–Si is chemically similar to the SiO_2–Si interface which is the ideal interface for MOS devices [10,11].

In this paper, a co-evaporation method that consists of E-beam evaporating HfO_2 starting material and resistance evaporating SiO pellets was used to dope the Si into the HfO_2 film to form the more thermal stable HfSiO film, and

* Corresponding author. Tel.: +86 29 83208210; fax: +86 29 83208210.
E-mail address: yangchen931@163.com (C. Yang).

http://dx.doi.org/10.1016/j.mssp.2014.05.044
1369-8001/

then the crystalline, optical and electrical characteristics of the HfSiO films were investigated and discussed.

2. Experimental

To deposit HfSiO thin films on the substrates of 2–4 Ω cm p-type Si(100) or fused quartz, a co-evaporation method, which was made up of an E-beam evaporator using HfO_2 (purity 99.99%) pellets as the starting material and at the same time a resistance heating evaporator using SiO (purity 99.99%) pellets as the staring material, were used in this experiments. The E-beam evaporator and the resistance heating evaporator were both located in the model ZZS-500 vacuum coating system (made by Chengdu Nanguang vacuum Technology Co. Ltd., China). Before the deposition, the Si substrates were ultrasonically cleaned by using acetone, and then thoroughly rinsed in de-ionized water. Finally, Si substrates were immersed in the diluted hydrofluoric solution ($HF:H_2O=1:10$) to remove the native SiO_2. During the deposition, the base pressure was less than 3×10^{-3} Pa, the working pressure was about 8.8×10^{-2} Pa with O_2 as the reacting gas, and the substrate temperature was automatically controlled at 200 °C by a heating system. The approximately 250 nm thickness of the deposited film was controlled using an optical thickness monitor. To obtain a film uniform in thickness, a sample holder rotating at a speed of 80 rpm was used. After deposition, the wafers were cut into several parts, and then were furnace annealed in N_2 at different temperature for 1 min. After that, Metal–insulator-semiconductor (MIS) capacitors were formed with aluminum top and bottom electrodes. The top electrode was prepared by electron beam evaporation at room temperature as a shadow mask with a diameter of 0.5 mm was used. All MIS capacitors were performed with rapid thermal anneal at 450 °C for 1 min in N_2 ambient to form ohm contact.

The films composition and chemical states were examined by X-ray photoelectron spectroscopy (XPS). Before XPS analysis, all samples were etched by argon ion for 1 min to clean the surface and thin the film. XPS spectra were calibrated with the binding energy (BE) of C 1s at 284.6 eV, and were fitted with computer assisted Gaussian–Lorentzian peak models. The crystals were analyzed by X-ray diffraction (XRD, X'Pert PRO MPD) using Cu Kα radiation. The optical characteristics were determined by a VU/vis/NIR0 spectrophotometer (Type Shimatzu UV/vis 3150) and an ellipsometer (Type J.A.WOLLAM M-2000UV). The leakage current density–voltage (*J–V*) and capacitance–voltage (*C–V*) of MIS capacitors was measured using precision semiconductor parameter analyzer (Type Agilent 4155C) and impedance analyzer (Type HP4294A), respectively.

3. Results and discussion

XPS analyses were used to determine the as-deposited HfSiO film composition and chemical bond. As shown in Fig. 1, Si 2p spectra were composed of three peaks at the binding energy of 101.56, 103.15 and 103.75 eV. Those peaks corresponded to different oxidized states of Si^{2+}, Si* and Si^{4+} respectively [12]. Among them the oxidation state Si* was originated from Hf–Si–O bonds [13]. The peak positions of O 1s peak located at 531.48 eV, lying between corresponding O 1s peaks of 530.4 eV in HfO_2 and 533 eV in SiO_2, indicated that Si–O bonds have influenced the Hf–O bonding characteristics because of the incorporation of Si in co-evaporation. Hf 4f spectra were shown in Fig. 1 with a characteristic peak of $Hf4f_{7/2}$ at the binding energy of 17.38 eV, which represented the formation of Hf–O bonds. However, due to the change of electron cloud distribution induced by the incorporation of Si, it was higher than that in HfO_2 [14]. Meanwhile, the peak of about 14.6 eV in binding energy that corresponds to Hf–Si bonds was not observed in the Hf 4f spectra, it demonstrated that the film is free of silicide. According to element sensitive factors and corresponding XPS peak area for the as-deposited film, the atomic ratio of Hf to Si was calculated to be around 4:1. The chemical composition of the film was $Hf_{28}Si_7O_{65}$.

XRD was employed to characterize the crystalline structure of the HfSiO films. The as-deposited films were amorphous. Fig. 2 illustrates XRD curves of HfSiO films annealed at 800, 850 and 900 °C for 1 min, respectively. It can be seen that the film annealed at 800 °C for 1 min showed a broad peak in the range of $2\theta\approx25^{o}$–35^{o} with a maximum intensity located at $2\theta\approx32^{\circ}$ manifesting an amorphous nature. The film annealed at 850 °C for 1 min had four peaks at $2\theta\approx24.7^{\circ}$, $2\theta\approx31.5^{\circ}$, $2\theta\approx35.3^{\circ}$ and $2\theta\approx50.6^{\circ}$ corresponding to the (110), (111), (200) and (220) planes of the tetragonal HfO_2 phase, respectively. With increasing the annealed temperature to 900 °C, the same four peaks were found with more pronounced shapes indicating better order of HfO_2 crystalline structure and a free of phase transformation. Usually, a transformation for HfO_2 film from the tetragonal phase to monoclinic phase occurred while the annealing temperature was as high as 800 °C [15]. However, in our case, a 900 °C annealing treatment only resulted in an increase of the intensities in the observed XRD peaks which all belong to the tetragonal phase. It could illustrate that the tetragonal HfO_2 phase in our samples was thermal stability. In addition, the tetragonal phase has a higher dielectric constant in comparison with the monoclinic phase. It demonstrated that the film could possess a higher dielectric constant even though it has been crystalline during a high temperature annealing process.

It is known that spectroscopic ellipsometry is a fast, sensitive and non-destructive method for film characterization. In our works, a four-phase optical model was used to investigate the HfSiO film. The model consists of the silicon substrate, a SiO_2 interfacial layer, an HfSiO layer, and a surface rough layer composed of a mixture of void space and HfSiO. Base on the best fit between the experimental and simulated spectra, optical constants (refractive index, *n*, and extinction coefficient, *k*) of the amorphous HfSiO film were extracted and illustrated in Fig. 3. To compare, the amorphous HfO_2 films were also measured by ellipsometry on the same model and the corresponding values of *n* and *k* were also presented in Fig. 3. About HfO_2 and SiO_2, it was known that the former has a higher *n* value of about 1.9 and, however, the latter has a lower *n* value around 1.45. So it was obvious that the *n*