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FT IR spectroscopy of nitric acid oxidation of silicon with hafnium oxide very thin layer

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ABSTRACT

Hafnium oxide is promising for future CMOS devices owing to wide band gap, good thermal stability on silicon, high permittivity and high refractive index. Infrared spectroscopy was used to study of the structural properties of 5 nm HfO_2 films after nitric acid oxidation (NAOS) of n-doped Si (1 0 0) substrates. Samples were annealed in N_2 atmosphere at different temperatures 200–400 °C for 10 min. For NAOS passivation 100% vapor of HNO_3 and 98% aqueous solution was used. The measurements revealed the formation of Hf-Si-O bonds depending on annealing temperature. The samples passivated in 98% aqueous HNO_3 solution showed spectra with more developed Hf–Si–O structures. Obtained FTIR spectra indicate the presence of monoclinic HfO_2 in amorphous layer in samples of A set and formation of cubic HfO_2 phase in amorphous layer with increasing of temperature. Infrared spectroscopy reveals the stable solid silicon oxide layer. The structural properties of HfO_2 are crucial for application in the future.

1. Introduction

Hafnium oxide is an interesting material for a broad range of applications. It can be uses as optical coatings for CCDs, antireflective multilayer coatings for night vision devices. Amorphous hafnium oxide has high dielectric constant (~16), relatively low leakage current, high band gap (~5.68 eV), and high transparency. Hafnium oxide has been extensively investigated as an alternative material to replace the silicon dioxide as the gate dielectric systems of microelectronic devices and reduce the leakage currents in the miniaturization of modern devices [1,2]. Hafnium oxide film can crystallize at a low temperature. The crystallinity strongly affects the permittivities of layer. Tetragonal and cubic high temperature phases have much higher permittivities (~70 and ~29 respectively [3]) in comparison with monoclinic HfO_2 (~16). So very thin starting SiOx is required to obtain layer nucleation and therefore cannot be avoided. On the other hand grain boundaries may provide paths for leakage current, resulting in the variation of electrical properties. To avoid this harmful effect silicon dioxide layer is used with HfO_2 [4]. To escape the formation of Hf-Si bonds and their negative effect on electrical properties is crucial to control their formation. Cheng et al. [5] found that post-deposition annealing can effectively eliminate the Hf–silicide formation. It is suggested that annealing accelerates the oxygen atoms diffusion, enhancing the oxidation of silicide and leading to silicate formation. The quality of layer is affected by reactions with the SiOx and/or silicon substrate. The result is silicate formation or regrowth of interfacial SiOx. To improve electrical properties of hafnium oxide/silicon oxide devices Iwamoto et al. [6] suggest continuous transition from HfO_2 to SiO_2 region. Therefore it is very important to study of the chemical states of interlayer and control its formation.

The aim of the study is observation of silicon oxide layer, its formation depending on post deposition annealing process and transformation of monoclinic HfO_2 in amorphous layer to cubic HfO_2 phase in amorphous layer with increasing of temperature.

2. Samples and methods

The Si wafers of n-type c-Si(1 0 0) were cleaned by standard RCA (Kern et Puotinen, 1970) method before formation of SiO_2 layers by NAOS technique. The thickness of this layer is 0.6 nm. Two sets of samples were passivated in HNO_3. Afterwards 5 nm hafnium oxide layer was deposited by atomic layer deposition (ALD) in oxidant water steam at 250 °C from tetrakis(dimethylamino)hafnium (TDMAH)–$Hf[N(CH_3)_2]_4$.

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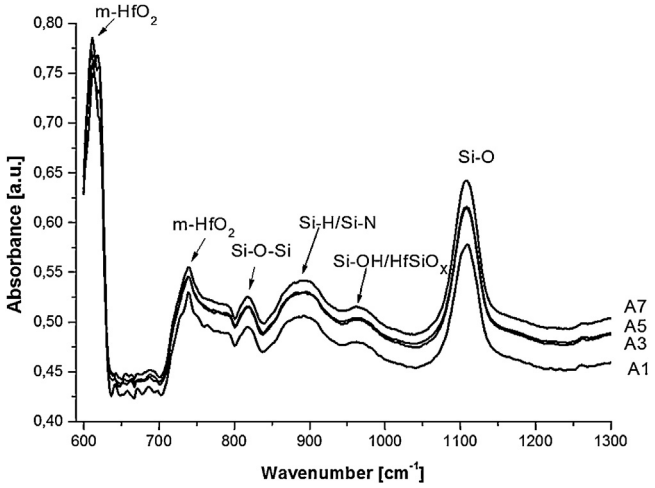

Fig. 1. Absorption IR spectra of set A of $HfO_2/SiO_2/Si$ sample in the range 600–1300 cm^{-1}. Spectra are not shifted.

A set: 100% HNO_3 – vapor
A1 – without annealing
A3 – annealed in N_2, 200 °C, 10 min
A5 – annealed in N_2, 300 °C, 10 min
A7 – annealed in N_2, 400 °C, 10 min

B set: 98% HNO_3 – aqueous solution
B1 – without annealing
B3 – annealed in N_2, 200 °C, 10 min
B5 – annealed in N_2, 300 °C, 10 min
B7 – annealed in N_2, 400 °C, 10 min

Samples were analyzed by FT-IR absorption spectroscopy (ATR-diamond technique) using Digilab Excalibur FTS 3000MX spectrometer in the range 4000–600 cm^{-1}, the resolution of 4 cm^{-1} and 60 co-added scans, for obtaining information on different types of bonding in the structures. Spectra were processed in Origin 6.0. **AFM** was performed on equipment Veeco CPII. The contact mode was used with the tip radius of 10 nm and the contact force of 100 nN.

3. Results

3.1. Description of the samples

In all investigated samples of A set in the range 600–1300 cm^{-1} six absorption bands are seen: around 600 cm^{-1} assigned to bulk Si phonon modes and m-HfO_2, absorption band at 695 cm^{-1} without absorption at 780 cm^{-1} is ascribed to cubic HfO_2, 738 cm^{-1} assigned to m-HfO_2, 818 cm^{-1} assigned to Si-O, broad absorption around 890 cm^{-1} assigned to Si–H/Si–N, broad absorption around 960 cm^{-1} assigned to Si–OH/$HfSiO_x$ and absorption at 1107 cm^{-1} assigned to Si–O (Fig. 1). Slight development of absorption around 600 cm^{-1} and 738 cm^{-1} is observed. All absorption spectra are almost similar even though the spectra of samples prepared with higher post-deposition annealing temperature reveal higher absorption spectrum in the whole investigated range.

To investigate the roughness of HfO_2 layer AFM measurements were done. We suggest that white areas are monoclinic phase of HfO_2 embedded in amorphous phase of HfO_2. The roughness of A1 sample is higher with more developed individual grains, probably monoclinic phase of HfO_2 (Fig. 2), in comparison with A7 sample (Fig. 3). Granularity of A7 sample is higher in comparison with A1 sample probably due to the presence of monoclinic and cubic phase of HfO_2.

In all investigated samples of B set six absorption bands are seen: around 600 cm^{-1} assigned to bulk Si phonon modes and m-HfO_2, absorption band at 695 cm^{-1} without absorption at 780 cm^{-1} is ascribed to cubic HfO_2, 738 cm^{-1} assigned to m-HfO_2, 818 cm^{-1} assigned to Si–O, broad absorption around 890 cm^{-1} assigned to Si–H/Si–N, broad absorption around 960 cm^{-1} assigned to Si–OH/$HfSiO_x$ and absorption at 1107 cm^{-1} assigned to Si–O

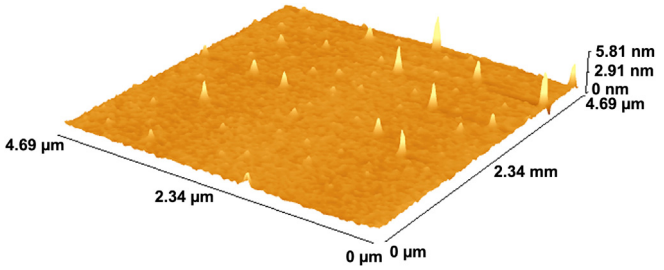

Fig. 2. AFM of $HfO_2/SiO_2/Si$ of A1 sample. RMS roughness is 0.23 nm.

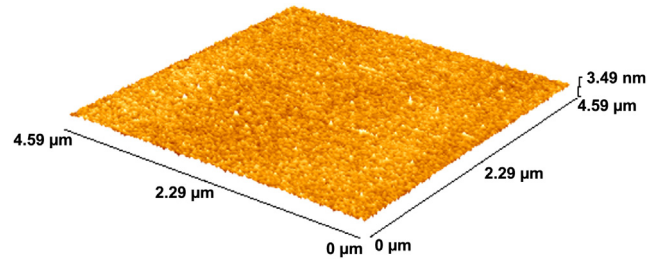

Fig. 3. AFM of $HfO_2/SiO_2/Si$ of A7 sample. RMS roughness is 0.15 nm.

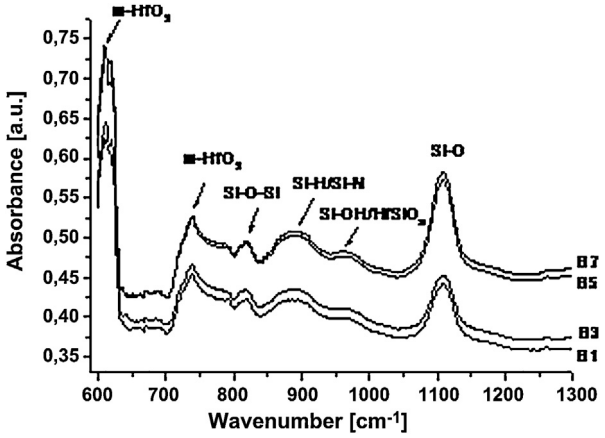

Fig. 4. Absorption IR spectra of set B of $HfO_2/SiO_2/Si$ layers in the range 600–1300 cm^{-1}. Spectra are not shifted.

(Fig. 4). Marked development of absorption around 600 cm^{-1} is observed. All absorption spectra are almost similar, but the higher post-deposition annealing the higher absorption spectrum in the whole investigated range is observed.

Investigating the roughness of HfO_2 layer by AFM measurements, the presence of monoclinic phase embedded in amorphous phase of HfO_2 was observed. The roughness of B1 sample (Fig. 5) is almost the same as roughness of B7 sample (Fig. 6). Granularity of B7 sample is higher in comparison with B1 sample probably due to

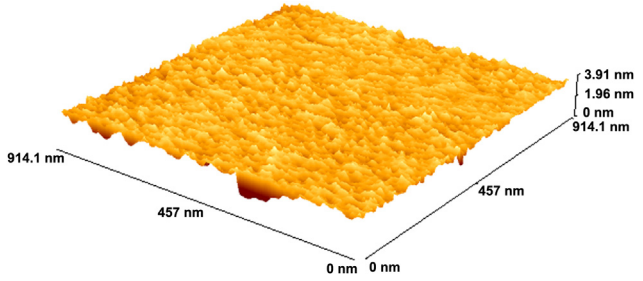

Fig. 5. AFM of $HfO_2/SiO_2/Si$ of B1 sample. RMS roughness is 0.23 nm.