Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2008) 4757–4761
applied surface science
www.elsevier.com/locate/apsusc

Application of spectroscopic photoemission and low energy electron microscope to high-k gate dielectrics: Relationship between surface morphology and electronic states during Hf-silicide formation

R. Yasuhara [a], T. Taniuchi [a], H. Kumigashira [a,b], M. Oshima [a,b,*], F. Guo [b,c], T. Kinoshita [b,c], K. Ono [b,d], K. Ikeda [e], G.-L. Liu [e], Z. Liu [e], K. Usuda [e]

[a] Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[b] Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, Kawaguchi, Saitama, 332-0012, Japan
[c] SPring-8/JASRI, Hyogo 679-5198, Japan
[d] Institute of Materials Structure Science, KEK, Tsukuba 305-0801, Japan
[e] Semiconductor Technology Academic Research Center, Kanagawa 222-0033, Japan

Received 2 November 2007; received in revised form 10 January 2008; accepted 18 January 2008
Available online 26 January 2008

Abstract

We have applied the spectroscopic photoemission and low energy electron microscope to study high-*k* gate dielectrics and have performed the following *in situ* operations during ultrahigh vacuum annealing: real-time observation of surface morphology and microregion photoelectron spectroscopy measurements. Changes in surface morphology and electronic states were consistent with the models previously reported in the case of HfO_2/Si. No clear differences between void regions and nonvoid regions have been observed in microregion photoelectron spectra for poly-Si/HfO_2/Si, regardless of phase separation in real space. These results have suggested that the initial void formation occurs in about 100-nm wide regions for both HfO_2/Si and poly-Si/HfO_2/Si.

Keywords: High-*k* gate dielectrics; Vacuum annealing; PEEM; Electronic states; Microregion photoelectron spectroscopy

1. Introduction

Recently, high dielectric constant (high-*k*) materials such as Al_2O_3, ZrO_2, HfO_2, and rare-earth oxides have been intensively studied as alternatives to SiO_2 which has long been used as gate dielectrics in ultralarge-scale integration (ULSI) metal-oxide-semiconductor field-effect transistors (MOSFETs) [1–6]. Among them, HfO_2 has been intensively studied and will be used in production starting in the near future as it satisfies the requirements for high-*k* gate dielectrics, that is, large valence-band and conduction-band offsets between high-*k* gate dielectrics and Si substrates, and high thermal stability at the interface with Si substrates, as well as a high dielectric constant.

However, it has been pointed out that the thermal annealing process after deposition leads to the degradation of its electrical properties. In particular, Hf-silicide formation is a serious problem. Thus, the mechanism of Hf-silicide formation has been investigated by photoelectron spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM) [7,8]. It has been reported in previous studies that the silicidation of HfO_2 involves local phase separation and a change in surface morphology [9,10]. In particular, the generation of voids with a diameter of about 1 μm in the initial reaction of Hf-silicide formation has been reported [10]. Furthermore, it is reported that the existence of poly-Si top electrodes affects the initial reaction mechanism of the silicidation [9]. Thus, it is important to investigate the electronic states of small regions (micron–submicron) and to compare them with surface morphology, in order to elucidate the mechanism of Hf-silicide formation for HfO_2/Si and poly-Si/HfO_2/Si, and to develop a new method of preventing silicidation reactions.

* Corresponding author at: Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, Tokyo 113-8656, Japan. Tel.: +81 3 5841 7191; fax: +81 3 5841 8744.
E-mail address: oshima@sr.t.u-tokyo.ac.jp (M. Oshima).

0169-4332/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.apsusc.2008.01.084

The spectroscopic photoemission and low energy electron microscope (SPELEEM) is a powerful instrument for the above-stated purpose. SPELEEM is equipped with a mercury lamp and an electron gun as excitation light and electron sources, respectively, combined with a hemispherical energy analyzer [11]. Changes in the surface morphology of thin films during annealing can be observed using the mirror electron microscope (MEM), that is, a special mode of the low energy electron microscope (LEEM) [12]. Furthermore, microregion photoelectron spectra can be obtained using the energy analyzer with synchrotron radiation. In this study, we have applied SPELEEM to the chemical reaction analysis of high-*k* gate dielectric HfO_2 thin films during annealing process in order to investigate the relationship between surface morphology and electronic states during Hf-silicide formation.

2. Experimental

We have prepared HfO_2 thin films on Si substrates with and without polycrystalline silicon (poly-Si) top electrodes. Schematic side views of the measured samples are shown in Fig. 1. The HfO_2 layers were deposited on clean *p*-type Si (0 0 1) substrates by reactive magnetron sputtering with Hf metal. The thickness was estimated, by elipsometry, to be 2 nm for the HfO_2 layer and 0.5 nm for the interfacial Hf-silicate layer on Si substrates. Poly-Si electrodes of 3 nm thickness were deposited on HfO_2 gate stacks at room temperature by magnetron sputtering. The quality of measured samples is almost the same as commercial samples. The experiments were performed using SPELEEM installed at BL17SU of SPring-8. Samples were annealed using a heater with electron bombardment in the analysis chamber under ultrahigh vacuum (10^{-9} to 10^{-8} Torr). In order to investigate the time evolution in MEM images and photoelectron spectra in detail, we have set the annealing temperature to be 700 °C and 550–600 °C for HfO_2/Si and poly-Si/HfO_2/Si, respectively. The annealing temperature was monitored with a thermocouple, which was carefully calibrated with the melting point of Pb (327.46 °C [13]) and the temperature of the phase transition of Si 7 × 7 to 1 × 1 surface reconstruction (around 900 °C [14]). *In situ* real-time observation of the surface morphology was performed in the MEM mode. Microregion photoelectron spectra were measured in the dispersion mode using selected-area apertures, the energy analyzer, and synchrotron radiation with the photon energy of 512 eV as the excitation light source. The total energy resolution was less than 0.4 eV. Details of this instrument are described elsewhere [15].

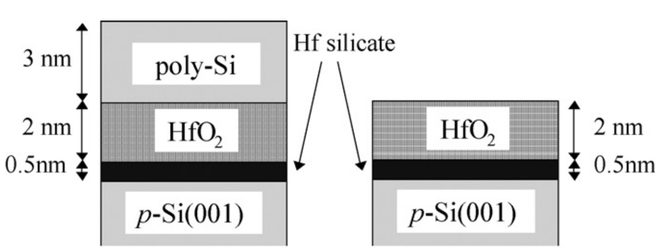

Fig. 1. Sample structures of poly-Si/HfO_2/Si (left panel) and HfO_2/Si (right panel).

3. Results and discussion

First, we present the results of HfO_2/Si without poly-Si top electrodes. The relationship between surface morphology and electronic states during Hf-silicide formation was observed. The annealing temperature was held at about 700 °C during the reaction. Fig. 2 shows annealing-time dependence of (a) MEM images with the field of view (FOV) of 15 μm diameter, (b) Hf 4*f*, and (c) Si 2*p* photoelectron spectra as (i) as-grown, (ii) initial stage, (iii) midstage, and (iv) further annealed stage of Hf silicidation during UHV annealing. Each circle in Fig. 2(a) indicates a selected-area aperture of 4.48 μm diameter. For the as-grown sample, a completely flat surface is observed in the MEM image and there are no Hf-silicide peaks in the spectra. At the initial stage, as shown in Fig. 2a(ii), voids with a diameter of 50–100 nm are observed as small white dots in the MEM image, and no Hf-silicide peaks are observed in the Hf 4*f* photoelectron spectrum. In addition, a peak located at around 103 eV in the Si 2*p* photoelectron spectrum, which corresponds to interfacial Si oxide, becomes broader toward lower binding energy. This implies the existence of suboxide generated by chemical reactions in the interfacial layer between HfO_2 and Si substrates. At the midstage (Fig. 2a(iii)), each void grows laterally. Accordingly, Hf-silicide peaks are clearly observed in the Hf 4*f* spectrum. The shoulder structure at the lower binding energy of Si 2*p* indicates silicide formation, and the intensity of the Si-oxide peak decreases at the same time. Further annealing roughens surface morphology throughout the thin film with the progress of Hf silicidation. These behaviors indicated by the MEM images and photoelectron spectra are consistent with the following proposed models. As pointed out by S. Stemmer [16] and S. Sayan et al. [17], SiO gas is generated at the initial stage of Hf silicidation, similarly to the SiO_2/Si system, which results in the formation of pinholes. The existence of suboxide and the absence of Hf-silicide at the initial stage seem to be the key in pinhole formation. These results imply that the pinhole-formation reaction involves Hf-rich Hf-silicate formation since the Si 2*p* suboxide peak intensity increases at the initial stage. The fact that the Hf 4*f* peak for Hf oxide at the initial stage (Fig. 2b(ii)) is broader than that at the as-grown stage (Fig. 2b(i)) strongly suggests the possibility of Hf-silicate formation. This situation is shown in Fig. 2a(ii), and this size of voids is consistent with the SEM results at the initial stage of void nucleation involving Hf silicidation, reported by N. Miyata et al. [10]. Our results show that each void grows up to several 100 nm in diameter with the progress of Hf silicidation, and thereafter, they combine with each other to cause roughness over the entire surface. This is thought to indicate the end of the void-formation step and the start of the entire Hf-silicidation step.

Next, we discuss the Hf-silicide formation in the poly-Si/HfO_2/Si structure. The annealing temperature was held at 550–600 °C during the reaction. We should mention here the difference of the temperature between HfO_2/Si and poly-Si/