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Crystallization in HfO_2 gate insulators with *in situ* annealing studied by valence-band photoemission and x-ray absorption spectroscopy

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Introduction

In the downscaling of complementary metal-oxide-semiconductor (CMOS) field effect transistor dimensions using a gate oxide thickness of less than 2 nm, conventional thermal SiO_2 is not applicable because of excess direct tunneling leakage current. HfO_2 has a high potential for the next-generation high-*k* gate insulator using merits such as considerably large energy-band gap, high dielectric constant and compatibility with conventional CMOS processes because of the thermal stability. However, the crystallization of the amorphous HfO_2 layer by annealing is one of the most serious problems during the CMOS device processing causing in a leakage current through the high-*k* insulators [1]. We have found that valence-band photoemission and x-ray absorption spectroscopy (XAS) are applicable for investigating the crystallization for HfO_2 gate insulator films including the interfacial layer since the electronic states are strongly affected by the crystal structure.

Experimental

Photoemission measurements were carried out at an undulator beam line BL-2C of the Photon Factory in High-Energy Accelerator Research Organization (KEK), where a high performance photoelectron analyzer (GAMMADATA-SCIENTA SES100) was equipped. The Hf-metal layer and the HfO_2 layer were deposited by DC sputtering using a Hf-metal target on the Si substrates at room temperature. We measured the sample having a HfO_2 layer of 3.9 nm and an interlayer of 1.7 nm as shown in the insets of Fig. 1 (a) [2].

Results and Discussion

Figures 1 (a) and (b) show annealing-temperature dependence in valence-band spectra and XAS spectra in HfO_2/Hf-silicate/Si structure. Insets also show schematic structures of the sample. Since the total oxide thicknesses in this experiment were 5.6 nm, the valence-band intensities from Si substrates between -1 eV and 3 eV of binding energy were considerably small. After the annealing at 800 ºC and 900 ºC, two components appear with the splitting of 3.0 eV around the binding energy of 5-9 eV as indicated by the solid triangles. In the XAS spectra, the absorption edge at 533 eV became sharp and additional peaks (solid triangles) appeared by the annealing at 800 °C and 900 °C in the higher energy region than the photon energy of 540 eV. The fact that sharp features and additional peaks caused by annealing are clearly observed is well correlated with the splitting in the valence band spectra. In order to elucidate the relationship between the change in spectral line shapes and crystallization, cross-sectional TEM images were observed after the annealing in UHV at 900 °C. As shown in Fig 1 (c), the amorphous structure at the as-grown stage [2] changed to the different images and some parts showed the crystallization in the HfO_2 top layer although the images in the interfacial layers remain unchanged as the amorphous structure. The TEM image reveals that the changes in both valence-band and O *K*-edge absorption spectra are related to the crystallization of the HfO_2 layer. Valence-band photoemission and x-ray absorption spectroscopy can be utilized to qualitatively investigate the crystallization features in high-*k* gate insulators [3].

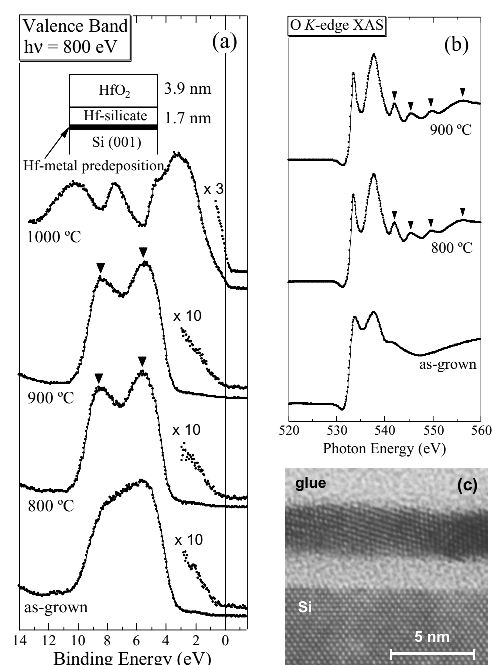

Fig. 1. Annealing-temperature dependence in valence-band spectra (a) and XAS spectra (b) are shown. (c) Cross-sectional TEM image after the annealing in UHV at 900 °C is also shown.

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