Crystallization with annealing in ZrO$_2$ gate insulators studied by photoemission and x-ray absorption spectroscopy

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1. Introduction
Due to the decrease in the size of complementary metal-oxide-semiconductor field effect transistors, a conventional SiO$_2$ gate oxide layer with less than 2 nm is not applicable because of excess direct tunneling leakage current. Consequently, alternative gate dielectrics with higher electrical dielectric constant (high-$k$) than SiO$_2$ are widely investigated. ZrO$_2$ is one of the promising candidates as high-$k$ dielectric materials for gate dielectrics. Although characteristics of ZrO$_2$ on Si have been extensively investigated [1], there remain serious problems to be solved such as the crystallization in ZrO$_2$ layers which promotes the leakage current through the crystallized grains after the annealing for activation. Although high-resolution core-level photoemission spectra are useful to reveal the precise chemical states due to the silicidation by the annealing above 860°C [2], the information about crystallization cannot be affected in core-level photoemission spectra. Therefore, we focus on the valence-band spectra and XAS to deduce the information about crystallization in the lower temperature range than that of the silicidation.

2. Experimental
ZrO$_2$ films were grown by a pulsed laser deposition (PLD) method using an ArF laser on hydrogen-terminated $p$-type Si(100) substrates. The thickness of the gate dielectric film was determined with ellipsometry to be 3 nm including the interface layer of 1 nm at the as-grown stage [3]. Photoemission spectroscopy using synchrotron radiation was performed at the undulator beam line BL-2C of the Photon Factory in High-Energy Accelerator Research Organization (KEK). The total energy resolution was about 0.35 eV at photon energy of 800 eV. Annealing was performed in ultra-high vacuum by the direct current flowing method through the samples. X-ray absorption spectroscopy was performed by a total-electron-yield made.

3. Results and discussion
Annealing-temperature dependence in valence-band spectra are shown in Fig. 1(a). The line shapes from $E_F$ to about -4 eV are identical to those of Si, meaning that this energy region is completely derived from the Si-substrate component. After annealing above 800°C, double-peak structures appeared with the splitting of 3.0 eV in the binding energy region of 5-9 eV. It may be related to the crystallization of the ZrO$_2$ layer by annealing. Thus, the O 2p non-bonding state may be clearly observed due to the changes in the chemical states since the crystallization from the amorphous structure promotes the changes to a sharp peak structure.

$O$ $K$-edge absorption spectra can be deconvoluted into two absorption edges for the ZrO$_2$ layer and the SiO$_2$ interfacial layer. The absorption edge around 532 eV is derived from ZrO$_2$, while that around 537 eV comes from the SiO$_2$ interfacial layer. The absorption edge at 532 eV became a sharp structure and additional peaks (solid triangles) appeared by annealing at 800 °C in the higher photon energy region than 540 eV. The fact that sharp features and additional peaks in XAS spectra are clearly observed by annealing is well correlated with the splitting in the valence-band spectra.

References
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