Chemical reaction and metallic cluster formation by annealing-temperature control in ZrO$_2$ gate insulator on Si

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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. Consequently, alternative gate dielectrics with higher electrical dielectric constant (high-$k$) than SiO$_2$ are widely investigated, such as transition-metal oxides, aluminates, and silicates. Among them, ZrO$_2$ is one of the candidates as high-$k$ dielectric materials for gate dielectrics. There are several reports on the thermal stability in ZrO$_2$/Zr-silicate/Si from the viewpoint of the chemical states using photoemission spectroscopy [1, 2]. However, it is strongly required to investigate the mechanism for the Zr-silicide formation by the annealing process. We report on the systematic annealing-temperature dependence of ZrO$_2$/Zr-silicate/Si structure using high-resolution synchrotron radiation photoemission spectroscopy.

**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 Organization (KEK) with photon energies ranging from 300 eV to 1000 eV, where a GAMMADATA-Scienta SES100 electron analyzer was equipped. The total energy resolution was about 0.35 eV and 0.15 eV at photon energies of 800 eV and 330 eV, respectively. Annealing was performed in ultra-high vacuum by the direct current flowing method through the samples (15 mm x 3 mm).

**Results and discussion**

Annealing-temperature dependence of Si 2$p$ core level is shown in Fig. 1 (a). Spectra are normalized at the height of Si 2$p$ bulk component. The sample-position dependence, i.e., the annealing-temperature dependence is also shown in the spectra annealed at 880°C. With increasing the annealing temperature, Si 2$p$ oxide components at the binding energy of 102.5 eV were depressed. First, the component of the Si-oxide layer is gradually suppressed by the annealing below 860°C, and then the annealing above 860°C caused no Si-oxide component.

Figure 1 (b) shows the annealing-temperature dependence of the Zr 3$d$ core level. By the annealing below 860°C, the spectral line shapes, which are fitted by a single component for each peak in the spin-orbit splitting, do not change. In the case of annealing above 860°C, new Zr 3$d$ peaks appear at the lower binding energy side, whose energy positions are explained by the Zr metal or Zr-silicide (ZrSi$_2$) formations. We note that the peak width of the metallic Zr component becomes smaller than that of amorphous ZrO$_2$, which suggests the crystallization of the metallic Zr atoms by annealing. The intensity ratio between ZrO$_2$ and metallic Zr changed systematically within the narrow temperature ranges. At 880°C annealing, the ZrO$_2$ component completely disappears. It is reported that the Zr 3$d$ peak position was shifted by the diffusion of Si atoms into the ZrO$_2$ layer [4]. Therefore, our results reveal that the Si atoms do not diffuse into the ZrO$_2$ layer by the annealing.

**References**


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