Interfacial reaction in ZrO_2/Si gate-stack structure probed by photoemission spectroscopy combined with combinatorial annealing system*

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We have investigated the mechanism of Zr silicidation from ZrO_2/Si gate-stack structure in ultralarge-scaled-integration devices by high-resolution core-level photoemission spectroscopy with annealing-temperature controlling. We have found that the interfacial SiO_2 layer thickness is tunable by controlling the annealing temperature and the silicidation occurs in the narrow annealing-temperature ranges. New method by combinatorial annealing system enables to control the narrow-range annealing temperature for the observation of the silicidation processes and to discuss the silicidation chemical reaction thermodynamically based on the annealing-temperature dependence in core-level photoemission spectra. [DOI: 10.1380/ejsnt.2006.263]

Keywords: ZrO_2/Si gate stack; silicidation; photoemission spectroscopy; combinatorial annealing

I. INTRODUCTION

Due to the downscaling 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, such as transition-metal oxides, aluminates, and silicates. Among them, 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 [1–5], there remain serious problems to be solved such as the Zr-silicate (ZrSi_xO_y or SiO_2) layer formation at the interface between the ZrO_2 layer and the Si substrate, the formation of metallic Zr silicide or Zr metal, and the crystallization in ZrO_2 layers which promotes the leakage current through the crystallized grains after the annealing for activation. If the chemical states and structures in ZrO_2 gate insulator change during thermal processes, electrical characteristics such as the threshold of gate voltage will be influenced drastically. To improve dielectric properties in gate insulators, the information about the chemical states for ZrO_2/Si gate stack structure has to be obtained explicitly including the inevitably formed interfacial SiO_2 layer.

High-resolution core-level photoemission spectroscopy is one of the most powerful techniques to investigate the chemical states for ultrathin gate insulator films. Especially, annealing-temperature dependence in photoemission spectra enables to discuss the chemical-reaction processes. Until now, we have found that the silicidation occurs in narrow-range annealing temperature

[6]. In order to investigate the mechanism of the silicidation in high- k insulator/Si gate stacks, annealing temperature has to be controlled explicitly in the narrow temperature ranges. In this motivation, we have developed the 'combinatorial' annealing system using the narrow-range heating-temperature gradient combined with synchrotron-radiation photoemission measurements. In this paper, we report on the annealing-temperature dependence in core-level photoemission spectra of $\text{ZrO}_2/\text{SiO}_2/\text{Si}$ gate-stack structure using combinatorial annealing system. Furthermore, we discuss the interfacial chemical reaction and the silicidation mechanism thermodynamically based on core-level photoemission spectra.

FIG. 1: Schematic view of the sample holder made by Molybdenum. For annealing at 880°C , temperature gradation in 20°C is also illustrated.

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FIG. 2: Core-level photoemission spectra in $\text{ZrO}_2/\text{SiO}_2/\text{Si}$ depending on annealing temperature. (a) Si 2p taken at $h\nu=330$ eV, (b) Zr 3d taken at $h\nu=800$ eV. In the spectra for the nominal 880 °C annealing, sample-position dependence corresponding to different annealing temperature is also shown. (c) Schematic views for each composition.

II. EXPERIMENTAL

$\text{ZrO}_2/\text{SiO}_2/\text{Si}$ gate-stack structure was grown by a pulsed laser deposition (PLD) method using ArF laser on hydrogen-terminated *p*-type Si(100) substrates [4]. The thickness of the as-grown gate dielectric film was determined to be 1.5 nm (ZrO_2) with an inevitable interfacial-layer formation of 1.5-nm SiO_2 at the as-grown stage, which is confirmed by the transmission electron microscope and core-level photoemission measurements [7].

In order to change the annealing temperature in narrow ranges, we developed the combinatorial annealing system. Figure 1 shows the schematic view of the sample holder made by molybdenum. The sample holder is consisted by two parts and isolated electrically by the ceramic parts. Edges in the sample are fixed by the metallic stopper. Current flowing through the sample heats just only the sample directly using high resistance of the Si substrate. Annealing temperature at the edge side is lower about 20 °C than that in the center, which is due to the cooling of the sample by the clamps. We monitored the annealing temperature for each sample positions using a pyrometer with the emissivity of Si (0.63). Annealing was performed under ultrahigh vacuum (UHV) conditions for 10 min at each temperature.

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) 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 at the photon energy of 800 eV. Synchrotron-radiation beam is focused to 0.5 mm $\times$ 0.1 mm size. By changing the focused beam spot from *1 to *4 as shown in Fig. 1, photoemission spectra depending on the narrow-range annealing temperature are measured.

III. RESULTS AND DISCUSSION

Annealing-temperature dependence of Si 2p core level is shown in Fig. 2 (a). Spectra are normalized at the height of Si 2p bulk component. The sample-position dependence, i.e., the combinatorial annealing-temperature dependence is also shown in the spectra of 880 °C annealing. With increasing the annealing temperature, Si 2p 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 com-

FIG. 3: Difference in Gibbs' free energy (ΔG) in reactions (i) $\text{ZrO}_2 + 6\text{SiO}_2 \rightarrow \text{ZrSi}_2 + 4\text{SiO}_2$, (ii) $\text{ZrO}_2 + 4\text{Si} \rightarrow \text{ZrSi}_2 + 2\text{SiO}$, and (iii) $\text{SiO}_2 + \text{Si} \rightarrow 2\text{SiO}$ depending on SiO-gas partial pressure under the reaction temperature of 800°C .

ponent.

Figure 2 (b) shows the annealing-temperature dependence of the Zr 3d core level. By the annealing below 860°C , spectral line shapes, which are fitted by a single component for each peak in the spin-orbit splitting, remain unchanged. In the case of annealing above 860°C , new Zr 3d peaks appear at lower binding energy side, whose energy positions are explained by the Zr-silicide (ZrSi_2) formations. We note that the peak width of the metallic Zr-silicide component becomes smaller than that of amorphous ZrO_2 , which indicates the crystallization of the metallic Zr-silicide by annealing. The intensity ratio between ZrO_2 and metallic Zr-silicide changed systematically within the narrow temperature ranges. By the annealing at 880°C , the ZrO_2 component disappears completely. It is reported that the Zr 3d peak position was shifted by the diffusion of Si atoms into the ZrO_2 layer [8–10]. Therefore, our results reveal that the Si atoms do not diffuse into the ZrO_2 layer by annealing.

Three important knowledges are derived from Fig. 2. First, the annealing below 860°C reduces the Zr-silicate layer thickness although the ZrO_2 layer was not affected by annealing. Schematic views in the sample are also shown in Fig. 2(c). Second, by the annealing at 860°C , the Zr-silicate layer was almost completely suppressed and therefore the ZrO_2/Si interfacial layer appeared. Third, by the annealing above 860°C , the metallic Zr-silicide components appeared with the small intensity of the surface component at the higher binding energy side. The silicide cluster formation was observed by the atomic force microscope as the cluster size of 20-nm diameter [6]. Therefore, the combinatorial annealing-temperature control in the narrow temperature ranges around 860°C can be practically useful for tuning the interfacial layer thickness. For $\text{Y}_2\text{O}_3/\text{Si}$ and HfSiON/Si gate stack structures, it is reported that the interfacial SiO_2 layer decomposition occurs before the high- k material decomposition [11, 12].

Next, we discuss the decomposition of the interfacial layer and the silicidation mechanism considering thermodynamics and chemical reactions. As the candidates of the interfacial chemical reaction, we propose the following reactions,

The SiO gas is related to each reaction [13–15]. Thermal stability in reactions (1)–(3) can be estimated thermodynamically using Gibbs' free energies. The Gibbs' free energies for these reactions depending on the SiO-gas partial pressure P_{SiO} at 800°C are shown in Fig. 3. In order to estimate the difference in Gibbs' free energy (ΔG) for each reaction, SiO-gas contributions are evaluated as the term for the gas, $-RT \ln P_{\text{SiO}}$ [13–15]. Interfacial reactions occur by following three steps. First, under the lower SiO-gas partial-pressure condition, the reaction (3) easily occurs at the interface between Si substrate and SiO_2 interfacial layer, which reduce the SiO_2 interfacial layer resulting in the generation of SiO gas and explain the changes in the photoemission spectral line shapes in the case of annealing at 860°C . Second, the generated SiO gas promotes the reaction (i) in higher SiO partial pressure region resulting in the Zr-silicide formation as products. The diffusion of the SiO gas into the ZrO_2 layer triggers the reduction of the ZrO_2 top layer. In addition, SiO_2 formed by the reaction (1) as a product will be reused in the reaction (3). Third, after the decomposition of SiO_2 interfacial layer, ZrO_2 layer directly contacts with the Si substrate, and then the reaction (2) accelerates the silicidation. Therefore, the mechanism of the silicidation is due to the reduction of the SiO_2 interfacial layer, which is revealed by the annealing-temperature dependence in core-level photoemission spectra.

IV. SUMMARY

We have investigated the mechanism of Zr silicidation from ZrO_2/Si gate stack structure by high-resolution core-level photoemission spectroscopy with combinatorial annealing-temperature controlling. We have found that the interfacial SiO_2 layer thickness is tunable by controlling the annealing temperature and the silicidation mechanism is related to the reduction of the SiO_2 interfacial layer, which is revealed by the interfacial chemical reaction thermodynamically based on the annealing-temperature dependence in core-level photoemission spectra.

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