

Photoemission Study on the Interfacial Reaction between Polycrystalline-Si Electrodes and HfO₂/Si Gate Insulators with *in-situ* Annealing

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Interfacial chemical reactions between HfO₂ gate dielectrics and polycrystalline-Si (poly-Si) electrodes during ultra-high vacuum annealing were investigated using synchrotron-radiation photoemission spectroscopy. High-resolution core-level spectra of Hf 4*f*, Si 2*p* and O 1*s* revealed that Hf silicide is formed at a much lower temperature for the poly-Si/HfO₂ interface than the HfO₂/HfSiO_x/Si interface, suggesting that a Hf-silicate layer plays an important role in suppressing Hf-silicide formation. Based on thermodynamical consideration, we propose a two-step reaction model at the poly-Si/HfO₂ interface.

Key words: synchrotron-radiation photoemission spectroscopy, polycrystalline-Si electrodes, HfO₂ gate stacks, annealing

1. INTRODUCTION

Recently, high dielectric constant (high-*k*) materials such as Ta₂O₅, SrTiO₃, ZrO₂ [1-6], and HfO₂ [5-9] have been extensively investigated as alternatives to SiO₂-based gate insulators. In particular, there has been much focus on HfO₂ to replace SiO₂ as a gate insulator due to the thermal stability, relatively high dielectric constant of 20-25[7-9], and wide band gap of 5.7-5.8 eV [7-9]. In parallel, a polycrystalline Si (poly-Si) has been used as gate electrodes for high-*k* gate dielectrics in order to extend conventional Si technology processes. The advantage in using poly-Si electrodes is that Fermi-level positions are tunable by carrier doping, resulting in the control of work functions. However, there remain serious problems, such as a thermal stability of the gate dielectrics in contact with poly-Si gate electrodes during high-temperature rapid thermal annealing in device fabrication. For ZrO₂ and HfO₂ high-*k* gate dielectrics, the silicidation at the poly-Si/ZrO₂ interface during high-temperature annealing has been observed [4,5]. The mechanism of the interfacial reaction between poly-Si electrodes and HfO₂/Si gate stacks has to be clarified from the viewpoint of the chemical bonding states at the interface. Photoemission spectroscopy using synchrotron radiation (SR) is the most powerful technique to elucidate the chemical bonding states including the interfacial region. Using SR photoemission spectroscopy, chemical reactions at the interface between HfO₂ and the Si substrate, called "lower interface" at various annealing temperatures, have been investigated [10]. It has been revealed that due to the chemical and thermal instabilities at the lower interface, the Hf-silicate interfacial layer is formed inevitably, and the interfacial reaction starts by annealing above 900°C. However, the chemical reactions at the interface between the poly-Si electrode and the HfO₂ layer, called the "upper interface," have not been thoroughly investigated to our knowledge. In this paper, we report on the annealing

effect at the poly-Si/HfO₂ upper interface systematically using high-resolution photoemission spectroscopy.

2. EXPERIMENT

The HfO₂ layer was deposited on clean *p*-type Si(001) substrates by dc sputtering using a Hf metal. The thickness was estimated by the ellipsometry to be 2 nm for the HfO₂ layer and 0.5 nm for the interfacial Hf-silicate layer on the Si substrate. A poly-Si electrode of 3 nm was deposited on the HfO₂ gate stacks.

Photoemission measurements were carried out at an undulator beam line BL-2C of the Photon Factory in the High-Energy Accelerator Research Organization (KEK), using a high-performance photoelectron analyzer (GAMMADATA-Scienta SES-100). The total energy resolution at room temperature was about 0.15 eV and 0.35 eV at the photon energy of 330 eV and 800 eV, respectively. The binding energies were calibrated by the Fermi edge of the gold. A sample surface was etched in a diluted HF solution to remove native oxide and contamination just before loading to the photoemission chamber. Annealing was performed in ultra-high vacuum (UHV) by flowing current directly through the samples before the photoemission measurements. Temperature at the sample surface was monitored by a pyrometer. Annealing was performed for 10 min at each temperature.

3. RESULTS AND DISCUSSION

Annealing-temperature dependence in Hf 4*f* and O 1*s* spectra taken at take-off angles of 0° (normal emission) and 60° is shown in Figs. 1 and 2. Hf 4*f* components of HfO₂ appeared at the binding energy around 18 eV with spin-orbit splitting [11,12]. Hf 4*f* spectra at a take-off angle of 60° showed broad line shapes, suggesting the Hf-silicate layer is formed in the surface region [10,13]. For the annealing at 700°C, at an emission angle of 60° compared with the normal emission configuration, the intensity ratio of the

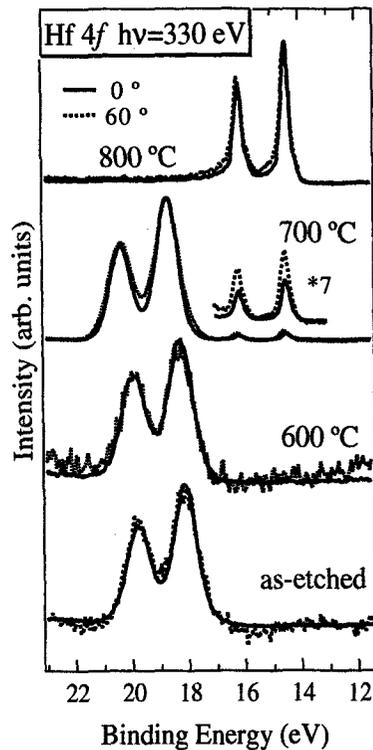


Fig. 1. Hf 4f ($h\nu=330$ eV) core-level spectra depending on the annealing temperature. Solid curves show the spectra taken at the emission angle of 0° . Dashed curves show those of 60° .

Hf-silicide component appearing at the binding energy of 14.5 eV [9,10] to the HfO_2 component increased.

The O 1s spectrum for the as-etched poly-Si/ HfO_2 /Si stack sample shows a broad line shape, which is due to the native oxide (SiO_2) on poly-Si and the HfO_2 layer. However, the 600°C UHV annealing almost successfully removed the native oxide, resulting in a narrow O 1s spectrum consisting of only a single component (HfO_2). The 700°C UHV annealing caused a shoulder peak or tail component (probably due to the Hf-silicate or SiO_2 component) at the higher binding energy of O 1s main peak corresponding to HfO_2 . This shoulder structure intensity is increased by the surface sensitive measurement at the 60° emission angle, suggesting the formation of Hf-silicate or SiO_2 at the "upper interface."

To investigate the interfacial reaction more precisely, Si 2p core-level photoemission spectra were measured at emission angles of 0° and 60° . As shown in Figs. 3 (a) and (b) for emission angles of 0° and 60° , respectively, the as-etched sample shows rather broad features for the Si 2p bulk component with some oxide components, which is due to the poly-Si electrode layer. Annealing at 600°C almost removes the surface native oxide since the oxide peak intensity is decreased, which is consistent with the O 1s features. However, annealing at 700°C drastically changed the Si 2p features. In the spectra taken at the 0° emission angle, the line shapes of the Si 2p main peak (bulk component) become quite sharp, suggesting that the poly-Si top layer is partially

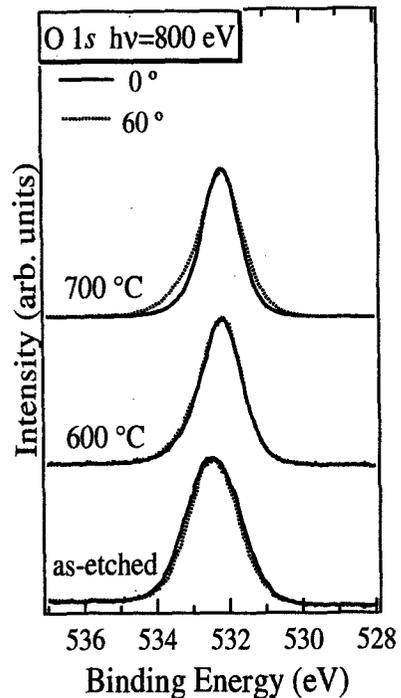


Fig. 2. O 1s ($h\nu=800$ eV) core-level spectra depending on the annealing temperature. Solid curves show the spectra taken at the emission angle of 0° . Dashed curves show those of 60° .

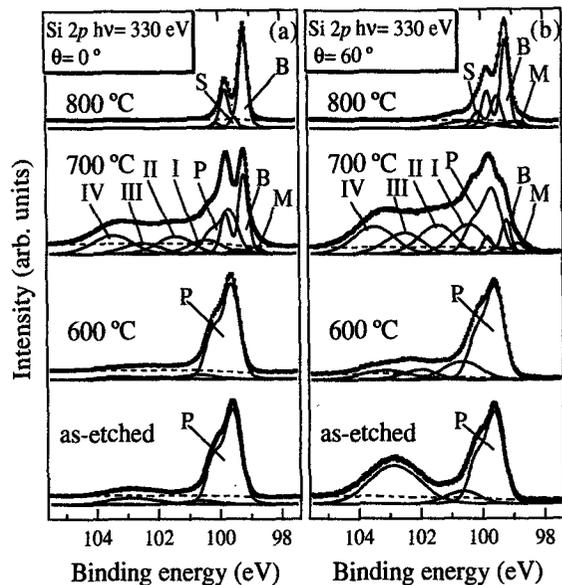


Fig. 3. Annealing-temperature dependence in Si 2p core-level spectra of poly-Si/ HfO_2 /Si taken at $h\nu=330$ eV. Take-off angles are 0° (a) and 60° (b). B, P, M, S, and I-IV show the components of bulk, poly-Si, Hf silicide, surface, and Si oxides, respectively.

removed and the Si-substrate component becomes detectable. These Si 2p spectra can be deconvoluted into eight components, i.e., B (bulk), P (poly-Si), M (metallic silicide), S (surface), and four sub-oxide components (I-IV). Sub-oxide components I-IV corresponding to

Si^{1+} - Si^{4+} are probably derived from the "upper interface" between poly-Si and HfO_2 , the Hf-silicate layer, and the "lower interface" between HfO_2 and Si substrates. The fact that Si^{1+} , Si^{2+} , and Si^{3+} component intensities are enhanced by surface sensitive measurement at the emission angle of 60° suggest these sub-oxide components may exist mainly at the "upper interface." Since the poly-Si layer is partially removed, it is thought that the Si^{4+} component exists in the Hf-silicate layer [10,14]. Furthermore, by annealing at 800°C , the Si oxide components have disappeared completely. This is a sharp contrast to the case without the poly-Si electrode, where the Hf-silicide formation occurs by annealing above 900°C [10].

Thus, the Hf-silicide and Hf-silicate formation occurs at the "upper interface" by annealing at as low a temperature as 700°C , although the interfacial reaction, especially the silicide formation, at the "lower interface" occurs by annealing at as high a temperature as 900°C in previous reports [10]. By annealing at 800°C , the HfO_2 component completely disappears and the metallic component appears. It is found that the Hf-silicide components are well fitted by a single component although the line shapes of the Hf silicide formed by the annealing of HfO_2/Si structures showed double peak structure consisting of the Hf-silicide component and most likely the surface component, which may be related to the surface morphology [15].

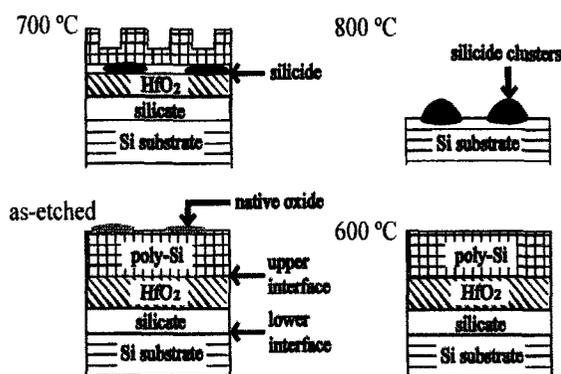


Fig. 4. Schematic view of samples annealed at each temperature.

Considering the above results, we constructed a model for the change in the poly-Si/ HfO_2 /silicate/Si stack structure by UHV annealing, as shown schematically in Fig. 4. By annealing at 700°C , the poly-Si electrodes are partially removed and the sample surface becomes rough. At the "upper interface," due to the direct contacts between HfO_2 and Si, Hf silicide and silicate are easily formed by the chemical reaction between HfO_2 and Si to form HfSi_2 and SiO gas. The Gibbs' free energy in this reaction is lower than that in the reaction between HfO_2 and SiO to form HfSi_2 and SiO_2 , at low SiO partial pressure. The SiO gas generated by this reaction triggers the reaction between HfO_2 and SiO which has the lowest Gibbs' free energy at high SiO partial pressure, resulting in the formation of SiO_2 in

HfO_2 , most likely in the form of Hf-silicate. Thus, the Hf-silicate and silicide compounds are formed. Furthermore, silicide clusters are formed on the Si substrates by annealing at 800°C [15].

4. CONCLUSION

A chemical reaction between HfO_2 and poly-Si at the "upper interface" starts by annealing at 700°C in UHV. As the results, Hf-silicide and Hf-silicate compounds were produced. The direct contact between poly-Si electrodes and HfO_2 promotes the chemical reaction for the Hf-silicide formation at much lower temperature at the "upper interface" than at the "lower interface."

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