Photoemission Study of HfO_2/Ge(100) Stacked Structures

Hiroshi Nakagawa, Akio Ohta, Hideki Murakami, Seiichiro Higashi and Seiichi Miyazaki
Graduate School of Advanced Sciences of Matter, Hiroshima University,
Kagamiyama 1-3-1, Higashi-Hiroshima 739-8530, Japan
E-mail: semicon@hiroshima-u.ac.jp

1. Introduction

Serious limitations in the continuous scaling of Si complementary metal-oxide-semiconductor (CMOS) devices lead to challenge to replace conventional materials in MOS structures with new ones such as metal gate, high-gate dielectric and advanced channel. Germanium is one of the most promising candidates for the channel material of advanced MOSFETs from the viewpoints of its higher carrier mobility than that of Si [1, 2]. Specifically, the combination of Ge channel and high-k dielectric stack is increasingly attractive because of its potential advantages of being able to realize a large driving current [3-5]. Because the thermal stability of the interface between high-k gate dielectric and Ge(100) is not understood clearly[6], the evaluation of chemical and electronic structures in ultrathin high-k gate dielectrics on Ge(100) after post-deposition anneal (PDA) is thought to be of crucial importance for practical use. In this work, we focus on ultrathin HfO_2/Ge(100) heterostructure and have studied chemical bonding features near the interface and the energy band alignment between HfO_2 and Ge(100) by using x-ray photoelectron spectroscopy.

2. Experiment

After degreasing by acetone and pure water rinse, Ge(100) substrates were immersed in 20%HCl solution to remove the native oxide. Subsequently, Ge(100) substrates were re-oxidized in 10%H_2O_2 solution at room temperature and dipped in a dilute HF-treatment. Subsequently, amorphous HfO_2 layers in the thickness range of 2.1~5.4nm were formed on wet-chemically cleaned Ge(100) substrates by electron-beam (EB) evaporation in O_2 ambient at room temperature. Some of the samples so prepared were annealed at 550°C in ultra-high vacuum (UHV) ambient at ~$1.0\text{x}10^{-6}$ Pa. To characterized the chemical bonding features in the oxides, high-resolution x-ray photoelectron spectroscopy (XPS) were performed at photoelectron take-off angles of 90° and 15° under a monochromatized AlK α (1486.7eV) radiation. The energy band profiles have been determined in combination of oxide bandgap values measured by O1s energy loss signals and the valence band lineups.

3. Results and Discussion

For as-evaporated sample, an increase in the chemically-shifted Ge3d signal due to Ge-O bonds is observable although the existence of the interfacial oxide layer between HfO_2 films and Ge(100) substrates is hardly detected by high-resolution TEM observations (Fig. 1). The result suggests that Ge atoms are diffused and incorporated into the HfO_2 network. To evaluate the diffusion of Ge atoms into the oxides, we measured Ge3d and Hf4f spectra of the as-evaporated sample at each step of progressive etching in a 0.1% HF solution. Obviously, the chemically shifted Ge3d signals due to Ge-O bonds and Hf4f signals were decreased when the sample was dipped in dilute HF solution for 10sec, which confirms the diffusion of Ge atoms in the oxide. After the complete removal of the top HfO_2 layer with dilute HF etching (60sec), the chemically shifted Ge3d signals show the existence of a Ge oxide layer as thin as ~0.4nm. As represented in Fig. 2, the compositional profile before and after UHV anneal at 550°C was obtained from the change in the core-line signals at each steps of oxide thinning. It is found that the Ge atoms were incorporated into the HfO_2 films by ~10at.% during the HfO_2 evaporation. In UHV annealing at 550°C, the Ge content was increased up to ~20at.% near the sample surface but no Ge atom was detected at the top surface. Notice that no compositionally separated layer was formed at the interface between HfO_2 and Ge(100) substrates. To evaluate the energy bandgaps of the ultrathin HfO_2 films before and after annealing, O1s energy loss

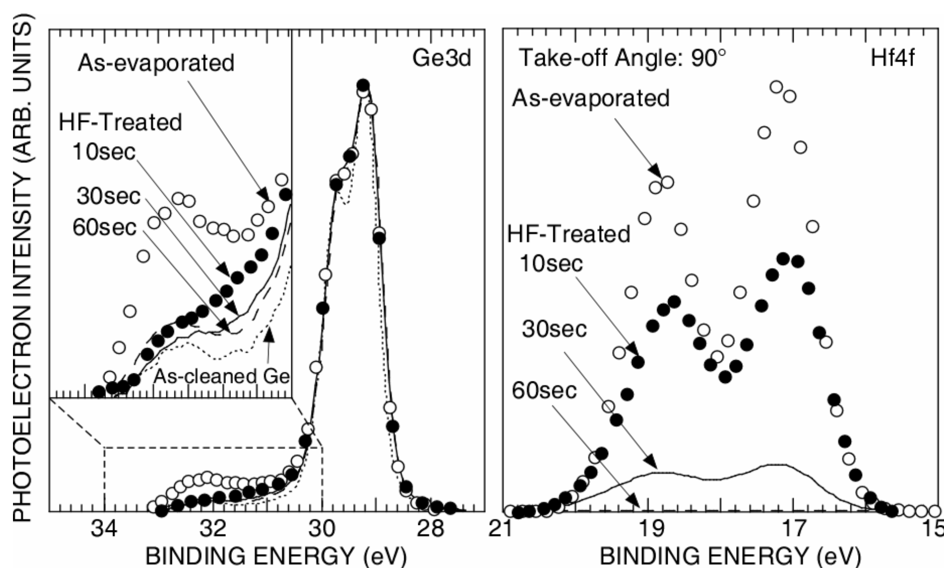

Fig. 1. Ge3d and Hf4f spectra measured at each oxide thinning for as-evaporated samples. The oxide thinning was performed by using a 0.1% HF solution.

signals were measured as shown in Fig. 3. Considering the fact that Hf4s signals overlap with energy loss spectrum of the primary O1s core line signals, we first subtracted the Hf4s component expected from Hf4f signal intensity from the measured spectrum to obtain an inherent background of the O1s core line signals and the defined the onset with a linear extrapolation of a leading segment to the background level. The energy bandgap of ultrathin HfO_2 in the thickness range of 2.1~5.4nm were determined to be 6.15±0.05eV and remain unchanged by UHV-annealing at 550°C. For the evaluation of the valence band (VB) offset between HfO_2 and Ge(100), the VB spectra for annealed sample were measured and deconvoluted into two components by subtracting the component originating from the wet-chemically cleaned Ge(100) as shown in Fig. 4. In the spectral deconvolution, the VB spectrum separately measured for wet-chemically cleaned Ge(100) was used and the binding energy for each valence band spectrum was calibrated with the Ge3d5/2 core line peak due to the metallic signals of the Ge(100) substrate. As a result, the VB offset between HfO_2 and Ge(100) was evaluated to be 3.35±0.05eV from the analysis of the VB spectra for HfO_2/Ge(100) structures and consequently the conduction band offset was derived as shown in Fig. 5.

In summary, we have confirmed that Ge atoms diffuse and incorporate into HfO_2 by HfO_2 evaporation and demonstrated that the energy band offsets between HfO_2: Ge and Ge(100) after UHV annealing at 550°C are ~3.35eV in the valence band edge and ~2.14eV in the conduction band edge, respectively.

Acknowledgements

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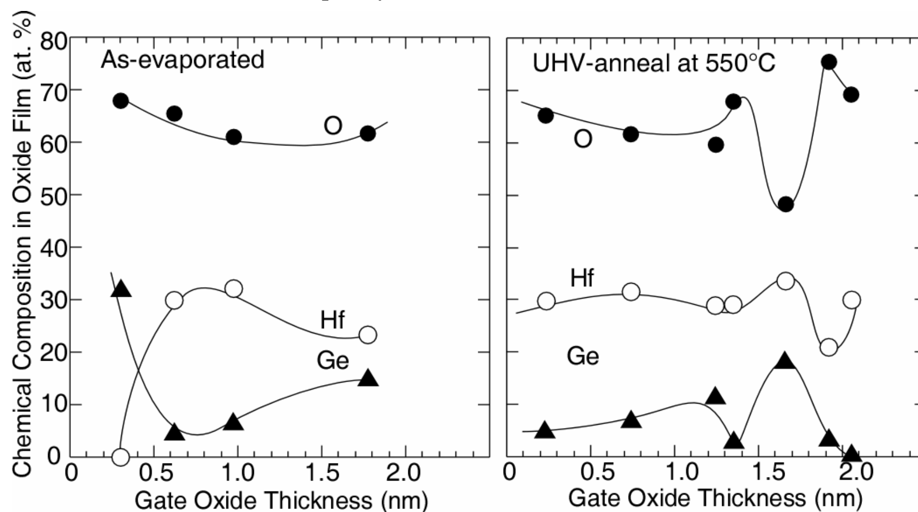

Fig. 2. the compositional profile (a) before and (b) after UHV anneal at 550°C was obtained from the change in the core-line signals at each steps of oxide thinning.

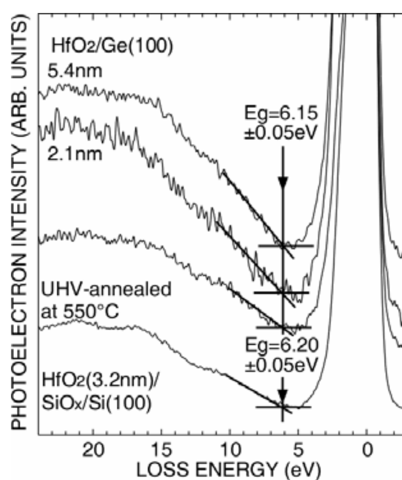

Fig. 3 O1s energy loss spectra for HfO_2/Ge(100) structures before and after UHV-anneal at 550°C. The spectrum for HfO_2/SiO_x/Si(100) structure was also shown as a reference. All spectra was subtracted the Hf4s component from the measured O1s energy loss spectra.

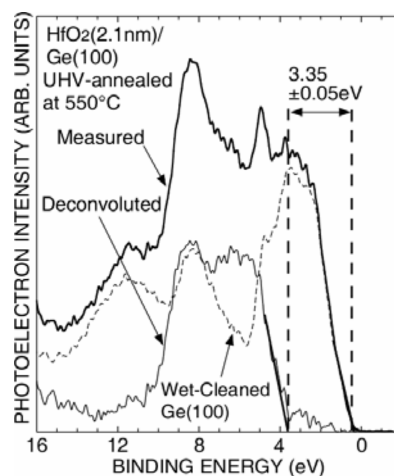

Fig. 4 Valence band spectra for annealed sample and the deconvoluted spectra for wet-chemically cleaned Ge(100). The remains correspond to the VB spectrum of the HfO_2 films.

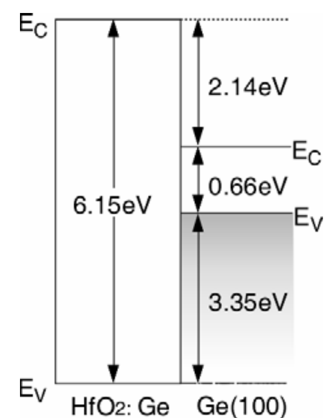

Fig. 5 Energy band alignment of HfO_2 incorporated Ge atoms to Ge(100) substrate.