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Evaluation of Effective Work Function of Pt on Bi-layer High-k/SiO_2 Stack Structure using by Backside X-ray Photoelectron Spectroscopy

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1. Introduction

Implementation of metal/high-k gate stack is strongly required to further increase in the capacitive coupling between gate and channel for advanced MOSFET [1]. For practical application to the metal/high-k gate stack, one of the most serious issues is to control of threshold voltage and to verify the origin of effective work function (WF) change in the gate stacks. So far, charge transfer from the dielectric to the metal gate attributable to oxygen vacancies in the dielectric layer has often been discussed as a possible origin of the effective WF change [2-4]. In addition, an electrical dipole layer at interface between high-k and interfacial SiO_2 has been suggested as a possible cause of the change in the effective WF [5, 6]. However, the detail mechanism of effective WF change and the contribution of electrical dipole layer at each interface have not been clearly understood yet.

Previously, it have been demonstrated that the back-side analysis by X-ray photoelectron spectroscopy (XPS) enables us to evaluate directly the metal WF value through the dielectric layer as well as chemical bonding features at metal/dielectric interface for the case with TiN/HfSiON/SiO_2 gate stack [7]. In this work, we have studied the effective WF of Pt on bi-layer high-k/SiO_2 and chemical bonding features near the interface between Pt/high-k and high-k/SiO_2 by using a back-side XPS technique.

2. Experimental

After conventional wet-chemical cleaning step of p-type Si(100), 1.0nm-thick SiO_2 was grown on Si substrate by thermal oxidation. Then, a bi-layer high-k stack consisting of 1nm-thick HfO_2 and 1nm-thick Al_2O_3 was deposited on SiO_2/Si by atomic layer deposition. Subsequently, a 50nm-thick Pt layer was formed as a gate electrode by sputtering, and followed by anneal at 400˚C for 30 min in ~3% H_2 diluted with N_2 to promote effective WF change. For the back-side analysis of the samples so prepared, the Si substrate was removed completely for ~1mm round by wet-chemical etching and high-resolution XPS measurements under monochromatized AlKα radiation were carried out from the back-side.

3. Results and Discussion

To evaluate the effective WF of Pt on bi-layer high-k/SiO_2 for back-side etched samples, the threshold energy of cut-off for photoemission near the low kinetic energy region was measured as shown in Fig. 1. In each spectrum, the threshold energy was determined precisely by curve fitting with a Fowler function in consideration of the thermal broadening in the metal Fermi surface [8]. The effective WF of Pt was measured to be 5.18±0.05eV through the HfO_2/Al_2O_3/SiO_2 (HAS) stack to be 4.95±0.05eV through the Al_2O_3/HfO_2/SiO_2 (AHS) stack.

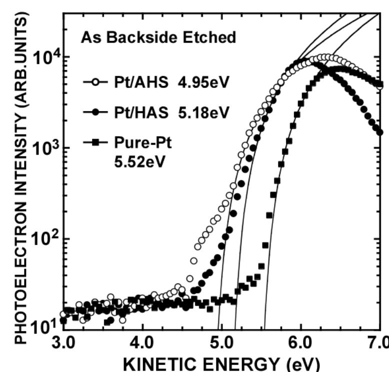

Fig.1 The yield spectra near the low energy cut-off for photoemission from Pt excited through bi-layer high-k/SiO_2 by monochromatized AlKα radiation for the back-side etched sample.

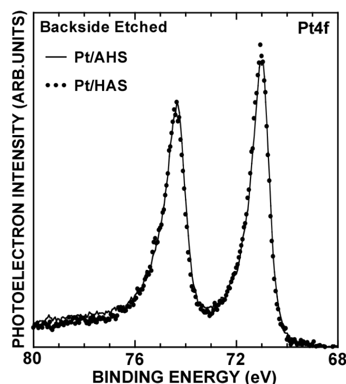

Fig.2 Pt4f spectrum for the back-side etched sample shown in Fig.1.

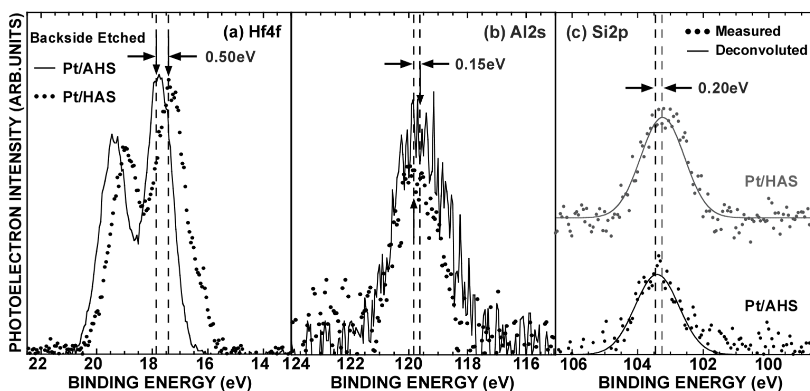

Fig.3 (a) Hf4f, (b) Al2s, and (c) Si2p spectra for back-side etched sample.

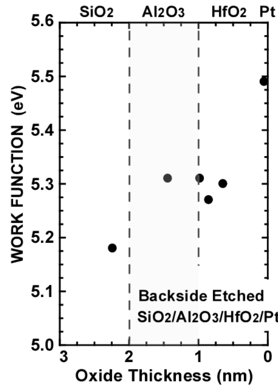

Fig.4 The yield spectra near the low energy cut-off for photoemission and measured effective WF values at each step of oxide thinning.

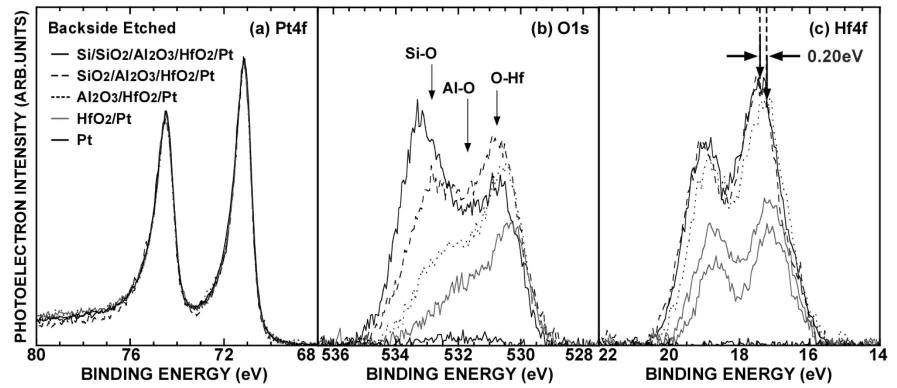

Fig.5 (a) Pt4f, (b) O1s and (c) Hf4f spectra for Pt/HAS stack structure with measured from back-side at each step of oxide thinning.

A considerable reduction of Pt WF from the measured vacuum WF value (~5.5eV) was confirmed in each of Pt/ bi-layer high-k/SiO_2 stack.

From Pt4f spectra for back-side etched samples shown in Fig. 2, no significant difference in chemical bonding features near the interface between Pt and bi-layer high-k stack can be detected. The core-line spectra for the sample of the Pt/HAS stack were shifted toward lower binding energy side as compared to the signals from the Pt/AHS stack (Fig. 3). The energy shift of Hf4f signals (0.5eV) was larger than Al2s case (0.15eV). If dipoles at the high-k/SiO_2 interface are only responsible for the Pt WF reduction, the energy shift seen in each core-line originating from the high-k layers should be the same as the WF change. But this is not the case. The result of Fig. 3 suggests that there exists some potential change in Pt/high-k aside from the high-k/SiO_2 interface.

To get an insight into the depth distribution of the inner potential change due to the electrical dipole layer and/or the fixed charges in the Pt/HAS structure, the back-side XPS were carried out at each step of oxide thinning (Fig. 4). The progressive oxide thinning was confirmed by the changes in core-line spectra from the dielectric layers (Fig. 5). From the analysis of the yield spectra near the low energy cut-off for photoemission at each oxide-thinning step shown in Fig. 4, the measured effective WF value of Pt was slightly increased by ~0.13eV with the complete removal of the SiO_2 layer. And, almost no change in the effective WF value near the HfO_2/Al_2O_3 interface was observable. By the complete removal of HfO_2 layer, the effective WF value was nearly identical to the vacuum WF value.

As shown in Fig. 5, Pt4f spectra show no change in the chemical bonding features near Pt/HfO_2 interface. By the removal of SiO_2 layer, Hf4f signal was slightly shifted by 0.2eV toward the lower binding energy side. This shift can be interpreted in terms of positive fixed charges in the SiO_2 side near the Al_2O_3/SiO_2 interface rather than the dipole layer at the interface. With further progressive oxide thinning, the energy shift of Hf4f signal was hardly detected. The result indicates that inner potential change in

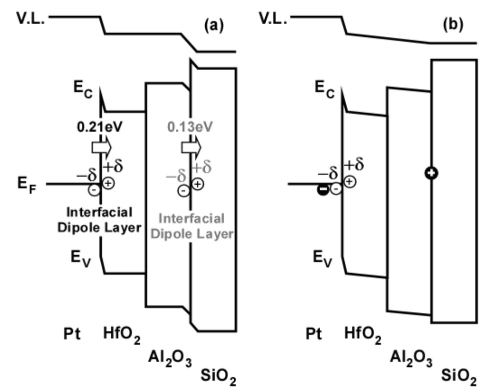

Fig.6 Energy band profile of Pt/HAS gate stack in consideration of (a) Al_2O_3/SiO_2 interfacial dipole layer or (b) Al_2O_3/SiO_2 interfacial positive fixed charge.

HfO_2/Al_2O_3 layer is negligible (Fig. 6). As a result, the dipoles at the Pt/HfO_2 interface, which involves the electron transfer from oxygen vacancies to Pt, contribute by 0.21eV to the Pt WF change, and positive fixed charges rather than the dipoles near the Al_2O_3/SiO_2 interface contributes by 0.13eV.

In conclusion, we have demonstrated that, from the back-side XPS analysis of Pt/bi-layer high-k/SiO_2 after H_2 anneal, the contribution of the dipoles at the Pt/high-k interface to the Pt WF change and the potential profile in the high-k/SiO_2 stack are quantified.

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