Study of Hafnium Related Oxide Thin Films for Advanced Gate Dielectrics Using Surface Analysis

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Hafnium-related thin oxide films have come to the attention of many institutions studying advanced gate dielectrics for field- effect transistors (FET) because the equivalent oxide thickness (EOT) demanded by the international technology roadmap for semiconductors (ITRS) is below the order of 1nm beyond 2006[1]. The requirement to investigate ultra thin films becomes more important as high dielectric constant (high-k) materials are promising to the gate dielectrics of advanced FET. We have investigated the physical properties of a high-k nano-laminate, consising of HfO_2 and SiN_x depending on a deposition process and an annealing process, using surface analysis. We used X-ray photoelectron spectroscopy (XPS) to determine the chemical state, the depth profile of each element and the band offset between high-k film and substrate. The depth profile was derived from angle resolve XPS (ARXPS) data using the maximum entropy method (MEM)[2, 3], which was developed proprietarily for this study. Elastic scattered electron energy loss spectra (ESEELS) were used to determine the band gap. ESEELS has strong advantages over the use of XPS for the sampling of hafnium-related oxide films because the peak shape is quite simple.

INTRODUCTION

High dielectric constant materials such as hafnium-related thin oxide films have been investigated as gate dielectrics for advanced metal oxide semiconductor (MOS) devices to meet the requirements for sub-65nm technology [1].

In this paper, we report that the physical properties of high-k films depend on the deposition and annealing process using surface analysis. The chemical state and depth profile are determined from XPS data. In particular, the depth profile is derived from ARXPS using a proprietary MEM calculation method. Band alignments of the interface between high-k film and substrate are determined from XPS valence band spectra and ESEELS. In particular, the adoption of ESEELS superiors to conventional methods based on XPS in determining the band gap.

EXPERIMENTS

After the Radio Corporation of America (RCA) standard cleaning with a final diluted HF dip, an interface silicon oxi-nitride layer (IFL) [0.5 nm] was grown on a silicon (100) substrate for all samples. Nano-laminate dielectric films composed form silicon-nitride (SiN_x) and hafnium oxide (HfO_2) multi layers are deposited on the IFL. The SiN_x film was deposited to use of thermal chemical vapor deposition (CVD) and the HfO_2 film was deposited to use of Atomic Layer Deposition (ALD), respectively. Stability of the ALD process is ensured using fluorescence X-ray spectroscopy. The details of the sample preparation and the evaluation conditions of XPS and ESEELS are described in Tables 1 and 2, respectively. The MEM software is proprietary, and was developed for this study. The performance is checked using thermal growth thin silicon oxide and

Table 1 Sample manufacturing process.

[1] p-Si(100) : substrate
[2] pre cleaning (native oxide fremoval)
[3] interface layer (IFL) growth [SiON]
[4] high-k deposition*
 1) $HfO_{2(45cycle)}$/IFL/$Si_{-sub.}$
 2) SiN/$HfO_{2(24cycle)}$/SiN/$HfO_{2(24cycle)}$/IFL/$Si_{-sub.}$
 3) SiN/$HfO_{2(16cycle)}$/SiN/$HfO_{2(16cycle)}$/IFL/$Si_{-sub.}$
 4) SiN/$HfO_{2(11cycle)}$/SiN/$HfO_{2(11cycle)}$/SiN/$HfO_{2(11cycle)}$/IFL/$Si_{-sub.}$
[5] anneal (800C in O_2)

*Details of deposition
 HfO_2(ALD) : $HfCl_4$+H_2O, 300C [0.07nm/cycle]
 SiN(LPCVD) : SiN_4+NH_4, 700C[0.29nm]

Table 2 Evaluation methods and measurement condition

[1] Chemical state analysis : XPS[PHI5400MC]
 Probe: Mg-kalpha, Analysis area : 1.1mmφ
 Pass energy : 17.9eV
 Takeoff angle : 90 deg.
 Energy step : 0.05eV/step
[2] Component depth profile : ARXPS [PHI5400MC] + MEM
 Probe: Mg-kalpha
 Pass energy : 17.9eV
 Takeoff angle : 24, 30, 37, 53, 64 deg.
 Energy step : 0.05eV/step
[3] Band alignment
 1) Band gap : elastic scattered electron spectrum [VG ESCALAB MKII]
 Probe: 500V, 2nA, Analysis area : 3.5mm×3.5mm
 Incident angle : 30deg., takeoff angle : 90 drg.
 2) Band offset : Valence band spectra [PHI5400MC]
 Probe: Al-kalpha(mono), Analysis area : 1.1mmφ
 Pass energy : 8.95eV
 Takeoff angle : 65 drg.
 Energy step : 0.05eV/step

silicon oxi-nitride films.

RESULTS AND DISCUSSION

Hf 4f spectra are directly reflected by the chemical state of dielectric films but the change of O 1s, N 1s and Si 2p spectra seem complex. This is because O 1s and N 1s spectra are influenced not only by the high-k layer but also by IFL and the thickness of the layers. Further, Si 2p spectra contain information about the high-k layer as well as IFL, the substrate, and thickness. Hf4f spectra and FWHM depend on process as is shown in Figs 1 and 2, respectively. A peak energy correction is applied using Si 2p(metal)=100 eV and the composition is defined by high resolution spectra, eliminate offing the substrate constituent, because the Si 2p spectrum involves a substrate component. The annealing process seems to reduce FWHM as a result of firming. The difference in composition doesn’t have an impact on FWHM. The peak shape of the HfO_2 sample is sharper than nano-laminates, as the peaks of

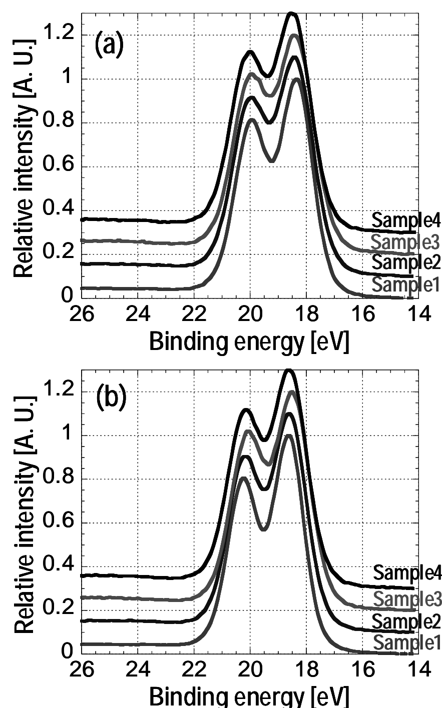

Fig. 1 Hf4f7/2 high resolution spectra depend on deposition process. (a)as deposited, (b)after anneal(800C).

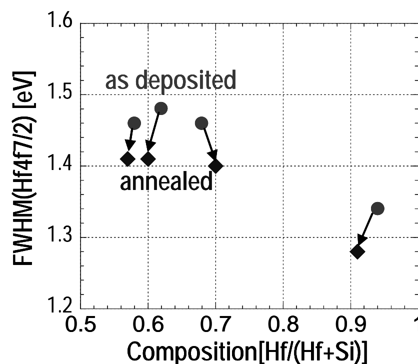

Fig. 2 FWHM of Hf4f7/2 depend on film composition and anneal process.

nano-laminates are composed of multiple peaks. The peaks of a deposited nano-laminated sample slightly broaden to the high binding energy side because of the remains of the ALD reaction in the sample and the peak shapes of the annealed sample broaden a little to the lower binding energy side as a result of the reaction of each layer.

Depth distribution profiles and the calculated composition of the high-k layer of each sample are shown in Fig. 3. The thickness derived from MEM seems reasonable, but the depth resolution of MEM is not enough to distinguish each nano-laminate structure and IFL layer. We think that the hydrocarbon contamination layer on top of the sample surface strongly affects the depth resolution

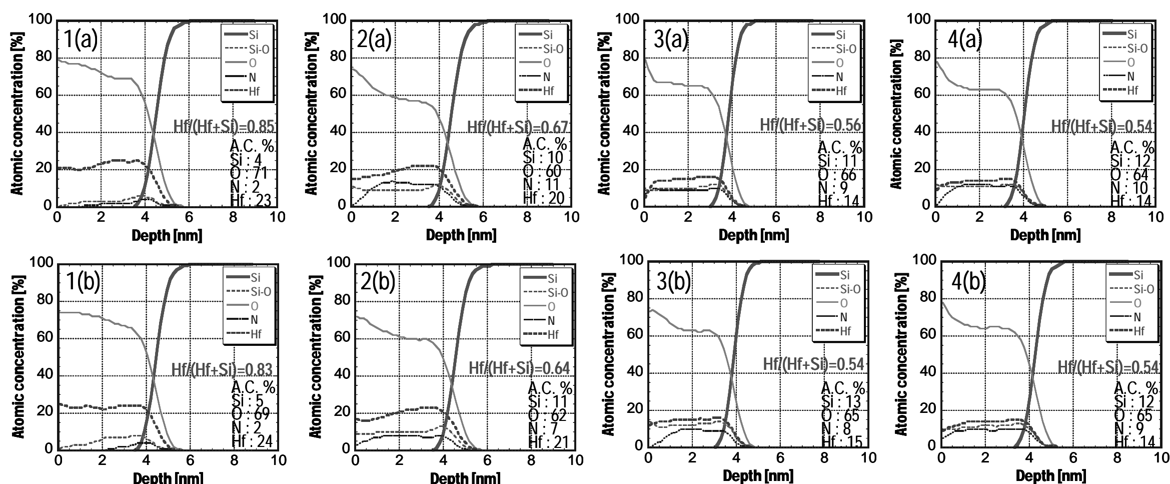

Fig. 3　Depth profile derived from ARXPS using MEM. 1(a) : sample1 as deposition, 1(b) : sample1 after anneal, 2(a) : sample2 as deposition, 2(b) : sample2 after anneal, 3(a) : sample3 as deposition, 3(b) . sample3 after anneal, 4(a) : sample4 as deposition, 4(b) : sample4 after anneal.

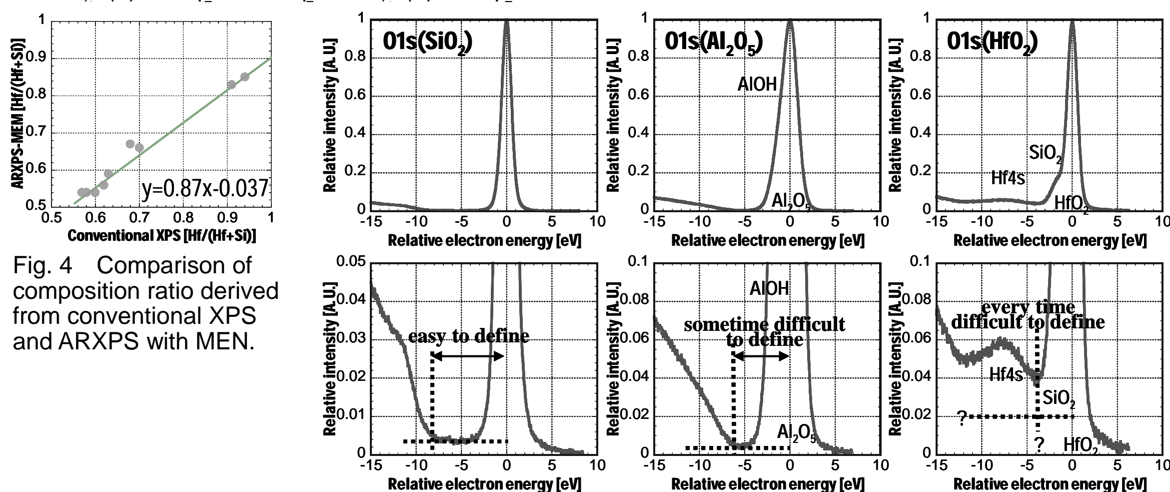

Fig. 4　Comparison of composition ratio derived from conventional XPS and ARXPS with MEN.

Fig. 5　The problem to define band gap using O1s spectrum. It is easy to define band gap to apply SiO_2 (a) but it is difficult to define band gap to apply Al_2O_3 and HfO_2 because O1s spectrum is composed from multiple peaks.

of the MEM calculation.The annealing process reduces nitrogen and promotes oxidation, and excess oxygen is going into the surface layer in all samples. The results of quantification using ARXPS-MEM show a good relationship with deposition condition and have a good relationship with conventional methods (Fig. 4).

The conventional procedures and principles to drawing the band diagram are shown in references [4][5][6]. We think the application of conventional procedures to define band gap has a fatal problem for hafnium oxide related materials because the Hf4s peak is overlapped on the onset of the energy loss spectrum and the O1s peak is formed from multiple chemical state peaks. Fig. 5 demonstrates a clear disadvantage in the use of O 1s (the conventional procedure). The O 1s spectrum is useful to determine band gap for SiO_2, but it is hard to evaluate results for Al_2O_3 and HfSiON. We have adopted ESEELS to solve this serious problem. The comparison of photoelectron spectra and ESEELS for HfSiON is shown in Fig. 6. ESEELS has the following extreme advantages over conventional methods to determine band gap : 1) Composed of only one simple (sharp) peak, 2) Lower background, 3) Reduction in the measurement time. The results of band offset determined from valence band spectra and band gap derived from ESEELS spectra are shown in Fig. 7.

To determine the band offset from XPS valence of the substrate. The contribution of the substrate is

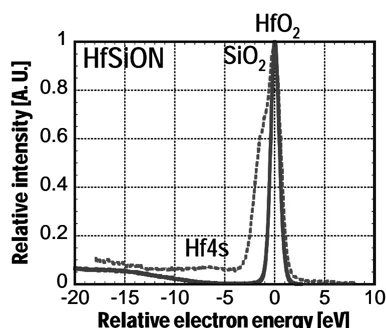

Fig. 6 Peak shapes comparison of O1s spectrum (doted line) and elastic scattered electron spectrum (solid line) from same HfSiON sample.

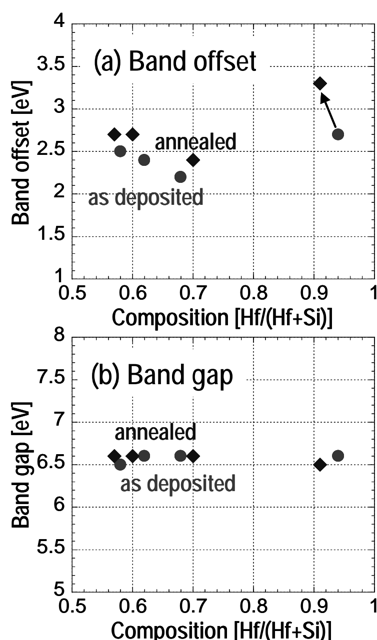

Fig. 7 Band offset and band gap depend on the composition and annealing process. (a) Band offset determine from valence band spectra, (b) Band gap derived from ESEELS. As deposited (circle), annealed (square).

estimated by measuring high-k removed substrates using a dilute HF solution. Consequently, band offsets (energy barrier of hole) increase with the annealing process but decrease with the augmentation of the Hf/[Hf+Si] ratio. Band gaps show no relation to the process. However, the energy barrier height of electron decreases with the annealing process but increases with the augmentation of the Hf/[Hf+Si] ratio.

CONCLUSION

We have examined the physical properties of hafnium oxide related nano-laminate (HfO_2/SiN_x…) films for gate dielectric films for advanced MOS devices using surface analysis. Transition of chemical states, composition depth profiles and band offsets were determined using XPS, and band gaps were derived using ESEELS. We have clarified the advantages of the use of ESEELS over conventional methods using photoelectron spectra to derive the band gap. The Hf/(Hf+Si) ratio has no influence on band gap but has an effect on band offset for nano-laminates.

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