Chemical Structures of HfO₂/Si Interfacial Transition Layer

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1. Introduction

The continuous shrinkage in dimensions of complementary metal-oxide-semiconductor device to achieve higher performance and low power consumption necessitates an continuous increase in gate capacitance while maintaining low leakage current levels. For this purpose a physically thicker high-K layer with high energy barriers for electrons and holes in substrate Si is necessary. Among the many candidate materials [1,2] HfO₂ has become promising materials due to its relatively high dielectric constant(>20),[3] high thermal stability[4] and high conduction and valence band offsets.[5-7] Although the structure and composition of HfO2 layer and interface between HfO₂ and substrate Si[8] and the chemical reactions between HfO₂ layer and substrate Si were studied,[9,10] the composition and chemical structures of transition layer between HfO2 and substrate Si have not been clarified yet. It will be shown in the present paper that high energy X-ray photoelectron spectros-copy(XPS) combined with high-resolution Rutherford backscattering(RBS) was effective in the accurate determination of compositional depth profile of transition layers between more than 4-nm-thick \hat{HfO}_2 film and substrate Si.

2. Experimental Details

 \hat{HfO}_2 layers used in this study were prepared as follows: 1) After the chemical oxide was formed on Si(100) in a $HCl/H_2O_2/H_2O$ solution, 4-nm-thick HfO_2 layers were formed by ALCVD using HfCl₄ and H₂O at 300° \tilde{C} .(named as sample A in the following) One of HfO₂/chemical oxide/Si(100) thus obtained was followed by the rapid thermal annealing in an nitrogen ambient at 1000 °C for 5 sec(abbreviated in the following as RTA).(named as sample B in the following). 2) After 1-nm-thick oxynitride layer was formed in NO ambient, 3-nm-thick HfO2 film was formed by ALCVD followed by annealing in N_2 ambient at 700 °C for 30 sec. HfO₂/oxynitride/Si(100) thus obtained was followed by RTA.(named as sample C in the following) Thicknesses of samples A, B and C were determined by spectroscopic ellipsometry. As a reference 1.3-nm-thick silicon oxide layer was formed in 1 Torr dry oxygen at 900 °C through 0.5-nm-thick peroxide layer, which was formed by oxidizing hydrogen-terminated Si(100) in 1 Torr dry oxygen at 300 °C.(named as sample D in the following)

High energy XPS, that is, excitation of Si 1s photo-electrons by 5950 eV photons with electron escape depth of 7.2 nm in HfO₂ was performed at a beamline(BL29XUL)[10] of SPring-8.

3. Experimental Results and Discussions

Figure 1 shows the depth profile of samples A and B determined by high-resolution RBS. According to this figure, Hf atoms diffuse toward substrate Si by RTA. Furthermore, the amount of Si atoms in HfO₂ layer increase slightly by annealing. This implies the RTA-enhanced diffusion of Si atoms from substrate Si into HfO2 layer. However, according to Fig. 2, such diffusion of Hf and Si atoms was almost suppressed by inserting oxynitride layer between HfO₂ layer and substrate Si.

As a result of diffusion of Hf and Si atoms through chemical oxide layer Hf silicate layer was formed between HfO₂ and Si substrate and Hf-Si bonds were formed at chemical oxide/Si interface as shown in the following. Si 1s spectra measured for samples A, B and C are shown in Fig. 3 and are compared with Si 1s spectrum measured for sample D. Si 1s spectrum arising from substrate Si measured for sample A is the same with that measured for sample D, while that measured for sample B is different from that measured for sample D. This change in Si 1s spectrum arising from Si substrate observed for sample B is caused by the RTA-enhanced diffusion of Hf atoms toward substrate Si, which produces Hf-Si bonds. On the other hand even after RTA Si 1s spectrum arising from substrate Si measured for sample C is almost the same with that measured for sample D, because in this case the diffusion of Hf atoms toward substrate Si is almost suppressed as shown in Fig. 2.

Analytical results of angle resolved photoelectron spectra measured for sample B, namely, Hf 3d spectral intensity($N_{\rm Hf}),$ Si 1s spectral intensity arising from transition layer(TL) between HfO_2 and substrate Si (N_{TL}) and RTA-induced change in Si 1s intensity arising from Si-Hf bonds (N_{Si-Hf}) , all of which are normalized by the sum of Si 1s intensity arising from substrate $Si(N_{bulk-Si})$ and that arising from Si-Hf bonds(N_{Si-Hf}), are shown as a function of photoelectron take-off angle. Solid curves are calculated using the depth profile of sample B shown in Fig. 5, while dashed curves are calculated using the depth profile of sample B shown in Fig. 1. Figure 5 is obtained by modifying Fig. 1 so as to explain the existence of Si-Hf bonds and SiO_2 in TL shown in Fig. 4. Excellent agreement between experimental data and calculated solid curves implies that the existence of Si-Hf bonds and SiO₂ near substrate Si indicated in Fig. 5 is plausible.

4. Conclusion

Compositional depth profile of transition layers between more than 4-nm-thick HfO_2 and substrate Si were accurately determined by combining high-resolution RBS with high energy XPS.

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Fig. 1 Depth profile of HfO₂/chemical oxide/Si(100) before and after Fig. 2 RTA determined by high-resolution RBS. dete



Fig. 3 Si 1s photoelectron spectra arising from HfO₂/chemical oxide/Si(100) before and after RTA, HfO₂/oxynitride/Si(100) after RTA and thermal oxide/Si(100).



Fig. 5 Depth profile determined so as to explain the existence of Si-Hf bonds and SiO₂ in TL shown in Fig. 4.



ig. 2 Depth profile of HfO₂/oxynitride/Si(100) after RTA determined by high-resolution RBS.



Fig. 4 Analytical results of angle-resolved spectra measured for HfO₂/ chemical oxide/Si(100) after RTA, namely, Hf 3d spectral intensity arising from HfO2 and Hf-Si bonds(N_{Hf}), Si 1s intensity arising from transition layer between HfO2 and substrate Si (NTL) and RTA-induced changes in Si 1s intensity arising from Si-Hf bonds(N_{Si-Hf}), all of which are normalized by the sum of Si 1s intensity arising from substrate $\mathrm{Si}(N_{\text{bulk-Si}})$ and that arising from Si-Hf bonds(N_{Si-Hf}), are shown as a function of photoelectron take-off angle. Solid curves are calculated based on the depth profile shown in Fig. 5, while dashed curves are calculated for N_{Hf} and N_{TL} based on the depth profile of HfO₂/ chemical oxide/Si(100) after RTA shown in Fig. 1. Here, it is assumed that the number of Si atoms contributing to Si-Hf bonds is equal to the number of Hf atoms contributing to Si-Hf bonds. If all Si atoms located within 2.1 nm from the surface are assumed to have chemical bonding only with oxygen atoms, dotted curves in Fig. 4 are obtained. Therefore, in order to explain the experimental data in Fig. 4 it is necessary to consider Si-Hf bonds located within 2.1 nm from the surface as shown in Fig. 5.