In-Depth Profile of Hf-Based Gate Insulator Films on Si Substrates Studied by Angle-Resolved Photoelectron Spectroscopy Using Synchrotron Radiation

S. Toyoda,[1,2,3*] H. Kumigashira,[1,2,3] M. Oshima,[1,2,3] G. L. Liu,[4] Z. Liu,[4] and K. Ikeda[4]
[1]*Department of Applied Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*
[2]*Core Research for Evolutional Science and Technology, JST, Bunkyo-ku, Tokyo, 113-8656, Japan*
[3]*Univ-of-Tokyo Synchrotron Radiation Research Organization, Bunkyo-ku, Tokyo 113-8656, Japan*
[4]*Semiconductor Technology Academic Research Center, Kohoku-ku, Kanagawa 222-0033, Japan*
[*]toyoda@sr.t.u-tokyo.ac.jp

(Received: January 18, 2009; Accepted: February 17, 2009)

We have investigated chemical-state-resolved in-depth profiles of HfO_2/SiO_x and $HfSiO/SiO_xN_y$ films using angular-dependent photoemission spectroscopy and Maximum-entropy method. Maximum-entropy method enables to reproduce the stack structure from angular-dependence of core-level spectra and it is utilized to determine atomic concentration of the interfacial layer. For the HfO_2/SiO_x film, it is elucidated that the Si^{+} and Si^{2+} sub-oxide components are located in the vicinity of Si substrate and Si^{3+} is distributed around the interfacial layer. In addition, annealing-temperature dependence of in-depth profile for the $HfSiO_2/SiO_xN_y$ film have been demonstrated, which reveals that Si oxide components diffuse from the interfacial SiO_xN_y layer into the HfSiO layer during annealing.

1. Introduction

Hf-based high-*k* gate insulator films are candidates for near-future CMOS devices because of applicable dielectric constant and reduction of gate-leakage currents [1]. Precise control of atomic concentrations and chemical bonding states in the films are essential to improve the characteristics of CMOS devices. Extensive experimental and theoretical investigations, especially for Hf-based high-*k* gate insulator films, have to be revealed that microscopic interfacial bonding states including sub-oxidized Si atoms can affect to the device performance. In order to probe the atomic concentrations and chemical bonding states along the depth, angular dependence in photoemission spectra is widely utilized for several SiO_xN_y and high-*k* gate insulator films [2]. However, it is difficult in conventional x-ray photoemission spectroscopy to resolve chemical states with high accuracy because of the broadening of the spectral line width since chemical shifts derived from interfacial sub-oxide atoms such as Si^{+}, Si^{2+}, and Si^{3+} are as small as 0.7-0.9 eV [3-8]. In addition, although angular dependence of the photoemission spectra qualitatively enables to give information on in-depth profiles, a numerical calculation technique to convert emission-angle profiles into in-depth profiles has to be established for quantitative analysis. In this study, high-resolution photoemission spectroscopy using synchrotron radiation has been performed on Hf-based high-*k* gate insulator films and chemical-state-resolved in-depth profiles are determined by maximum-entropy method (MEM), which is one of the well-known techniques to analyze the depth profile from angular-dependent photoemission spectra [2,9-11]. Algorism of the MEM was coded according to the previous report [11,12].

2. Simulation

In the typical statistic analysis, the least-square method is applied for the data analysis. However, a unique solution is not obtained principally because there are two problems such that (i) input data is finite and involves experimental error and (ii) information from the deep region is lost because the magnitude of photoelectron escape depth is nanometer order. The MEM analysis, which selects one "feasible" in-depth profile that well describes the angular-dependent data, is utilized to solve these problems. It is well known that the MEM analysis involves the process of maximizing joint function combined least-square term and entropy term with regularizing coefficient:

$$Q = 0.5\chi^2 - \alpha S, \qquad (1)$$

where Q is an objective function, χ^2 is a least-sqauare term, and S is an entropy term [10]. We have to minimize the value of Q to obtain the depth profile using MEM analysis. However, an ambiguity in the parameter of α, which is a Lagrange multiplier, brings the different output and

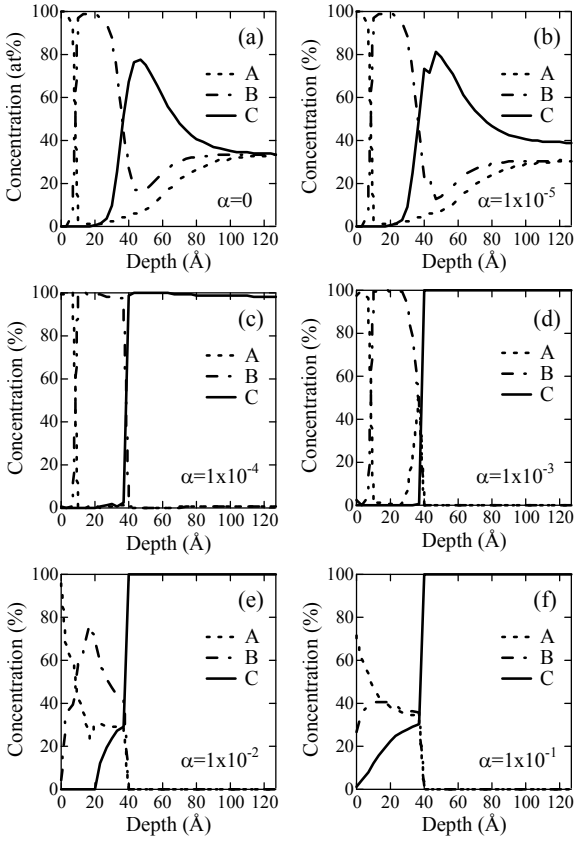

Fig. 1 Simulation for a typical stack structure by MEM analysis with the different values of α. In-depth profiles are shown with α=0 (a), α=1x10^{-5} (b), α=1x10^{-4} (c), α=1x10^{-3} (d) , α=1x10^{-2} (e), and α=1x10^{-1} (f).

the way to determine the value of α is still controversial in MEM analysis [10]. Therefore, in order to test the algorism, simulation of the MEM analysis was performed to reconstruct the structure of the stack film as shown in Fig. 1. The stack structure was assumed as 10 Å top-layer of element A and 30 Å interlayer of element B on the substrate of element C. Initial guess profiles were set to be homogeneous for each component. At first, it was attempted to deduce in-depth profile from these test data using the least-square method. After χ^2 was minimized, surface-atomic concentrations were well reproduced although it was not possible to reproduce the substrate component as shown in Fig. 1 (a). Thus, since the least-square method could yield physically extrinsic results, the minimization function should be replaced to the combination of χ^2 and *S*. Figures 1 (b)-(f) show the results with the different values of α from 1 x 10^{-5} to 1 x 10^{-1}. For the condition of α = 1 x 10^{-4}, both the surface and the substrate components were appropriately reproduced. Figure 2 shows the relationship between χ^2, -*S,* and $0.5\chi^2$ - α*S* as a function of α. It is found that both χ^2 and –*S* become constant in the range of 10^{-4} – 10^{-3} in α. The larger α values than

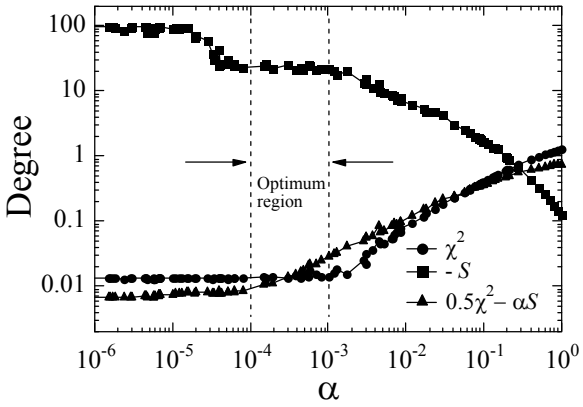

Fig. 2 The relationship between χ^2, -*S*, and $0.5\chi^2$-α*S* as a function of α. Optimum values of α were indicated from 10^{-4} to 10^{-3}.

optimum region lead to the biased results since the entropy term is enlarged resulting in strongly model dependent results. On the other hand, in the case of smaller α values, this analysis corresponds to least-square method. Suitable α value is estimated as the optimal region since both χ^2 and -*S* are constant and they do not depend on the model term within this region. In order to obtain the suitable α value, the optimization of α as shown in Fig. 2 is necessary. The optimum region of the α value is not changed in this procedure if we modify physical parameters for type of materials such as probing depth and sensitivity factor.

3. Experiments

A HfO_2/SiO_x stack film was also grown on H-terminated Si substrates at the substrate temperature of 600 ºC by metal organic CVD methods using $Hf[N(CH_3)_2]_4$ under NO gas ambient for oxidizing. A $HfSiO/SiO_xN_y$ film were deposited on clean *p*-type Si (001) substrates by atomic layer deposition. The physical thicknesses of HfSiO layers were estimated to be 2 nm by the elipsometry. A SiON interfacial layer of 0.7 nm exists between the HfSiO(N) film and the Si substrate. The $HfSiO/SiO_xN_y$ sample was annealed at 850 °C and 1050 °C for 1 minute at pressures of N_2 gas by the direct current flowing method through the sample. The temperature at the sample surface was monitored by a pyrometer. Cross-sectional transmission electron microscopy (TEM) and Rutherford backscattering spectrometry (RBS) were performed to precisely determine the total film thickness and the atomic concentration, respectively. Photoemission spectroscopy was carried out at an undulator beam line BL-2C of the Photon Factory in High-Energy Accelerator Research Organization (KEK). The total energy resolutions were 0.15 eV using hν = 630 eV photons for Si 2*p*, N 1*s* and Hf 4*f*

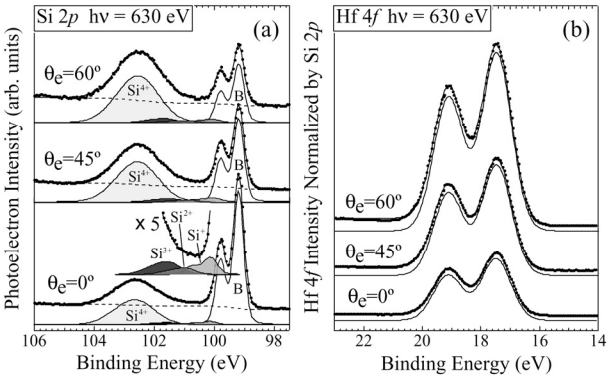

Fig. 3 Photoemission spectra of Si 2*p* (a) and Hf 4*f* (b) core levels in the HfO_2/SiO_x stack film depending on the emission angle. Curve-fitting results are also shown.

core-levels. Emission angle of photoelectrons was changed from the surface normal to 60° for enhancing the surface sensitivity. Curve fitting for core-level photoemission spectra was performed by a standard nonlinear least squares fitting procedure using a Voigt function convoluting Gaussian and Lorentzian functions.

4. Results and Discussion

Figure 3 shows Si 2*p* (a) and Hf 4*f* (b) core-level spectra for the HfO_2/SiO_x stack film measured at the photoelectron emission angles of 0º, 45º and 60º with the photon energy of 630 eV. The binding energies at each panel were calibrated by referring position of Si $2p_{3/2}$ bulk levels as 99.20 eV. The fitting results show that Si 2*p* spectra were deconvoluted into five components, i.e., B (bulk), Si^{1+}, Si^{2+}, Si^{3+}, and Si^{4+} components. With increasing the emission angle (θ_e), the components of Si^{x+} (x=1,2,3,4) in the Si 2*p* spectra and the intensities of Hf 4*f* spectra are relatively enhanced compared to the B component, which is well consistent with the stack structure of HfO_2/SiO_x on the Si substrate. In-depth profile of the HfO_2/SiO_x stack films is determined by simulating angular dependence of core-level intensity using the MEM analysis. Figure 4 (a) shows atomic concentration in-depth profile revealing that the HfO_2 layer is

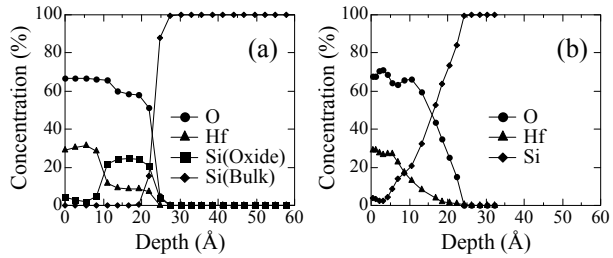

Fig. 4 In-depth profiles of the HfO_2/SiO_x stack film calculated by MEM analysis (a) and in-depth profile obtained by RBS measurements (b).

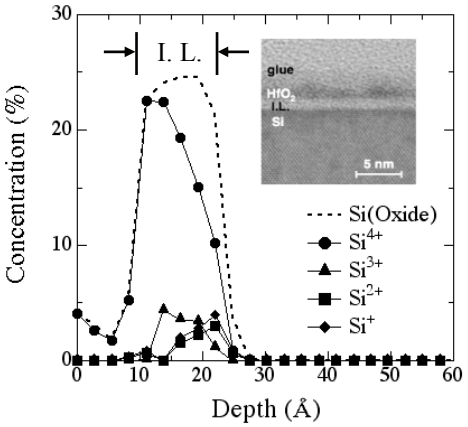

Fig. 5 Sub-oxide-resolved in-depth profiles of the HfO_2/SiO_x stack film. Inset shows cross-sectional TEM images of the stack film suggesting double layer structures.

distributed in the surface region and the composition of the interfacial layer is Hf-silicate. The MEM analysis is utilized for evaluating the atomic concentrations in the gate stack films on the Si substrate. The in-depth profile by MEM analysis is quantitatively coincides with RBS although there are slight differences in oxygen profiles at the surface and Si profiles at the interface. Chemical-state-resolved in-depth profile of HfO_2/SiO_x stack film is presented in Fig. 5. Si^+ and Si^{2+} components are located in the vicinity of the Si substrate and the Si^{3+} component is distributed around the interfacial layer as denoted in the inset. Concentrations of the Si^{x+} components are higher than the SiO_2/Si system [3], and distributed around the SiO_2 film region. This results show that top HfO_2 layer may degenerate the interfacial SiO_2 structures during the film growth process.

For the application of MEM analysis, we have also investigated changes in the atomic concentration in-depth profile during the annealing process. Since there are several problems to be solved in high-temperature annealing processes for dopant activation such as silicidation of HfO_2 and an increase in the equivalent oxide thickness, it is important to examine annealing-temperature

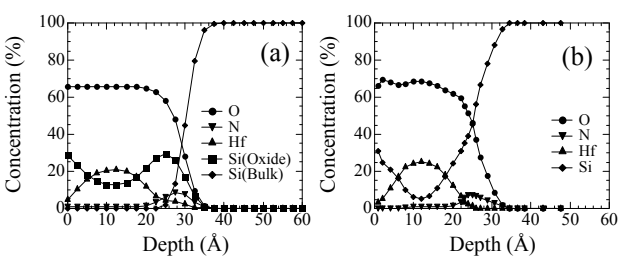

Fig. 6 In-depth profiles of the $HfSiO/SiO_xN_y$ stack film calculated by MEM analysis (a) and in-depth profile obtained by RBS measurements (b).

dependence of the chemical structures in the Hf-based high-*k* gate insulator films. Figure 6 (a) shows in-depth profiles in the $HfSiO/SiO_xN_y$ stack film by MEM analysis at the as-grown stage. The in-depth profile showing a complicated layer structure reveals that the SiO_2 layer is distributed in the surface and interface region and nitrogen atoms are slightly distributed at the interfacial layer, which is also confirmed by RBS measurements as shown in Fig. 6 (b). Nitrogen concentration is different between MEM and RBS at the interface. Figure 7 shows annealing-temperature dependence of in-depth profiles in the $HfSiO/SiO_xN_y$ stack film. It should be noted that changes in the in-depth profiles suggest that Si oxide components diffuse from the interfacial SiO_xN_y layer into the HfSiO layer and concentrations of Hf relatively decrease. It is possible that oxidation of the Si substrate occurs by residual oxygen in N_2 ambient [13]. These structural changes affect electrical properties of the gate insulator film such as capacitance, leakage current, and carrier motilities [14]. As mentioned above, fabrication process of interfacial layers becomes more important for the next-generation device using high-*k* gate insulators on the Si substrate. These analyses consequently would be utilized to investigate the relationship between chemical structures and device characteristics.

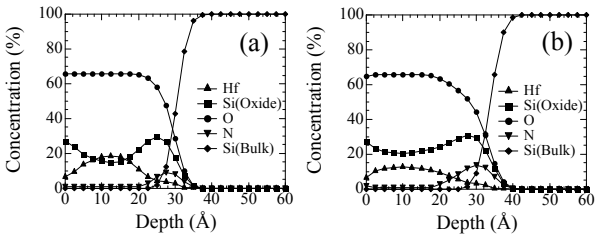

Fig. 7 Annealing-temperature dependence of in-depth profiles in the $HfSiO/SiO_xN_y$ stack film; (a) 850 °C and (b) 1050 °C at the N_2 pressure of 100 Torr.

5. Conclusion

In conclusion, angle-resolved photoemission spectroscopy and the MEM analysis have been performed on the HfO_2/SiO_x and $HfSiO/SiO_xN_y$ stack films to determine in-depth profiles. Atomic concentration in-depth profiles reproduce the stack-structures. Compared to conventional techniques of in-depth profile analysis, the merit of this method is chemical-state-resolving with high resolution such as second nearest neighbor atoms and sub-oxide components. By combination of high-resolution synchrotron radiation photoemission and the MEM analysis, it is possible to reveal in-depth chemical structures of gate dielectrics in the near-future CMOS devices for improving device characteristics by immediate feedback.

6. Acknowledgement

The authors would like to thank the Semiconductor Leading Edge Technologies, Inc., (Selete) for providing the high-*k* gate dielectric samples. This work was supported by the Semiconductor Technology Academic Research Center (STARC). The synchrotron-radiation photoemission measurements were performed under the project 05S2-002 at the Institute of Materials Structure Science at KEK.

7. References

[1] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).
[2] J. P. Chang, M. L. Green, V. M. Donnelly *et al*., J. Appl. Phys. **87**, 4449 (2000).
[3] J.-H. Oh, H. W. Yeom, K. Hagimoto *et al*., Phys. Rev. **B 63**, 205310 (2001).
[4] J. Ushio, T. Maruizumi, and K. Kushida-Abdelghafar, Appl. Phys. Lett. **81**, 1818 (2002).
[5] Y. K. Kim, H. S. Lee, H. W. Yeom *et al*., Phys. Rev. B **70**, 165320 (2004).
[6] M. Oshima, K. Kimura, K. Ono *et al*., Appl. Surf. Sci. **216**, 291 (2003).
[7] S. Toyoda, J. Okabayashi, H. Kumigashira *et al*., Appl. Phys. Lett. **83**, 5449 (2003).
[8] S. Toyoda, J. Okabayashi, H. Kumigashira *et al*., Appl. Phys. Lett. **87**, 102901 (2005).
[9] K. Nishizaki, H. Nohira, K. Takahashi *et al*., Appl. Surf. Sci. **216**, 287 (2003).
[10] R. L. Opila and J. Eng Jr., Prog. Surf. Sci. **69**, 125 (2002).
[11] A. K. Livesey and G. C. Smith, J. Electron Spectrosc. Relat. Phenom. **67**, 439 (1994).
[12] S. Toyoda, J. Okabayashi, M. Oshima *et al*., Surf. Interface Anal. **40**, 1619 (2008).
[13] H. Kamada, T. Tanimura, S. Toyoda *et al*., Appl. Phys. Lett., 93, 212903 (2008).
[14] I. Oshiyama, K. Tai, T. Hirano, *et al*., Jpn. J. Appl. Phys. **47**, 2379 (2008).