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Silicate layer formation at $HfO_2/SiO_2/Si$ interface determined by x-ray photoelectron spectroscopy and infrared spectroscopy

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A high-k Hf-silicate interfacial layer grown by the solid phase reaction between sputtered metallic Hf films and an underlying SiO_2/Si substrate through *in situ* vacuum annealing and subsequent thermal oxidation has been investigated. By means of the chemical shifts of Si 2p, Hf 4f, and O 1s core-level spectra determined by x-ray photoelectron spectroscopy (XPS), the formation of an interfacial Si-O-Si bond as the dominant reaction during *in situ* thermal oxidation of the $Hf/SiO_2/Si$ gate stack has been confirmed. *In situ* vacuum anneals without air exposure at 700 °C accelerates the interface reaction and results in the formation of Si-rich Hf-silicate interfacial layer. Analysis by Fourier transform infrared spectroscopy (FTIR) has indicated that vacuum annealed samples containing the silicate interface layer effectively suppresses the growth of the interfacial SiO_x layer compared to unannealed samples during postdeposition annealing. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2361161]

I. INTRODUCTION

With the downscaling of complementary metal-oxide-semiconductor (CMOS) device dimensions over the past decade, high-dielectric-constant (k) gate dielectrics have been extensively investigated as an alternative to conventional silicon dioxide or oxyniytides, which faces its scaling limits due to excessive gate tunneling current and intrinsic reliability in the coming generations. Among these high-k materials reported to date, hafnium oxide, one of the most promising candidates, is under intense investigation due to its relatively high dielectric constant (~25) and superior thermodynamic stability when in direct contact with Si.[1–3] However, many issues, such as interfacial layer formation, the low crystallization temperatures (<500 °C), the high permeability to oxygen, and boron penetration during the deposition/post-annealing processing causes equivalent oxide thickness (EOT) scaling and reliability concerns.[4,5] Recently, despite its lower permittivity some particular attentions have been focused on hafnium silicate pseudobinary alloy owing to its desirable properties, including its larger bandgap, heavier effective mass for electron tunneling,[6] reasonable stability against crystallization, and lower leakage current than HfO_2 with the same EOT.

Currently, some researches have focused on the fabricating of Hf, Zr-silicate gate dielectrics at the dielectric/Si interface. Watanabe observed that the zirconium silicate formed by self-organized reactions is formed at the interface of ZrO_2/Si.[7] Kirsch *et al.* investigated the fact that hafnium silicate produced by sputtering and annealed at 600 °C in N_2 ambient is formed at the interface of HfO_2/Si.[8] However, the hafnium silicate intermixing has not been detected at the ALD-HfO_2/Si interface.[9]

Among various deposition techniques, atomic-layer deposition (ALD) has been considered to be the only feasible method to control thickness down to the nanometer range and composition of metal oxide ultrathin films in a layer-by-layer fashion.[10] However, the existence of residual impurities in the deposited film by ALD due to the use of a precursor is unfavorable to the quality of HfO_2 gate oxide.[11] From the viewpoint of gate stack fabrication, although current research has been concerned with "depositing" high-k dielectrics on the substrates, we think that high-quality films should be prepared by "interface reaction" just like oxidation at SiO_2/Si. Recently, the solid phase reaction between sputtered metal and the SiO_2 underlayer has been proposed to fabricate La silicate and Zr silicate.[12,13] Compared to other deposition methods, the potential advantage of a solid phase reaction is that it would allow the well-developed SiO_2/Si interface to be retained in the processing and promise better and less contaminated dielectric/Si interface.

In this paper, we describe Hf-silicate dielectrics fabricated by solid phase reaction between sputtered ultrathin metallic Hf layer and SiO_2 underlayer. By means of characterization from x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR), we investigate the chemistry of the $HfO_2/SiO_2/Si$ interface of oxide gate stacks systematically and confirm the formation of hafnium silicate.

II. EXPERIMENTAL DETAILS

The n-Si (100) wafers with 4–12 Ω cm resistivity were ultrasonically cleaned in mixed solution ($NH_4OH:H_2O_2:H_2O$) and then thoroughly rinsed. In this treatment the native

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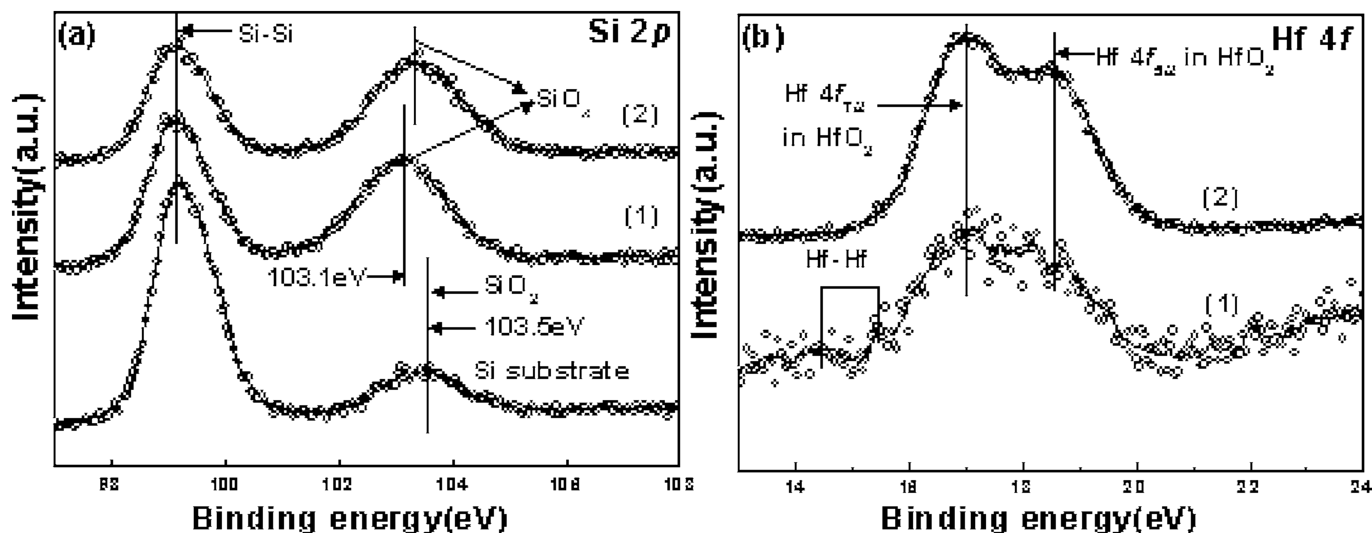

FIG. 1. XPS spectra of the as-deposited Hf/SiO_2/Si (1) and 400 °C thermal oxidized Hf/SiO_2/Si samples (2). (a) Si 2*p* core-level patterns and (b) Hf 4*f* core-level patterns. The bottom spectrum in (a) was obtained from a 1.5 nm thick SiO_2 layer on Si.

amorphous SiO_2 layer with 1.5 nm thickness measured by spectroscopic ellipsometry remains on the substrates. First, ultrathin pure metal Hf layers in the range of 3–5 nm thickness were formed using radio-frequency sputtering under ultrahigh vacuum condition at room temperature. After metal precursor deposition, *in situ* thermal oxidation of the metal precursor films was performed at 400 °C under 1×10^{-3} Pa oxygen pressure. For some samples, an *in situ* high vacuum anneal ($<5\times10^{-5}$ Pa, 700 °C) was performed to promote the solid phase reaction between Hf and the SiO_2/Si substrate after Hf deposition, and then *in situ* thermal oxidation. *Ex situ* XPS was performed by using the ESCALAB MK II (VG, UK) system, equipped with an Mg $K_\alpha$radiation source (1486.6 eV) and hemispherical analyzer with a pass energy of 20 eV. Effects of experimental charging were corrected by setting the C 1*s* peak for adventitious carbon at 284.6 eV, and shifting the entire spectrum correspondingly. Nonlinear Gaussian lineshapes were used for spectral profile deconvolution. Analysis of the interfacial layer between the sputtered ultrathin metallic Hf layer and SiO_2 underlayer in relation to post-deposition annealing was carried out by using Fourier transform infrared spectroscopy (FTIR) in a Nicolet Magna 750 operating in transmission mode.

III. RESULTS AND DISCUSSION

A. XPS characterization

Figure 1 shows XPS spectra obtained from samples of Hf metal layers deposited on SiO_2/Si substrate; as-deposited and *in situ* thermal oxidation at 400 °C. From Si 2*p* core level spectra shown in Fig. 1(a), it can be seen that a chemical shift originating from the 1.5 nm SiO_2 is confirmed. However, after Hf metal precursor deposition, the Si 2*p* peak, corresponding to SiO_2, shifts toward lower binding energy, from 103.5 to 103.1 eV. This can be contributed to the reaction of the initial chemical SiO_2 layer on the Si substrate with the deposited Hf metal layer and the formation of an interfacial suboxide $SiO_{x<2}$.[14] Comparing the Si peak of the Si substrate in Fig. 1(a) with Fig. 1 (1) and (2), from the as-deposited Hf and 400 °C thermal oxidized sample, respectively, we find that the intensity from Si is reduced in the latter. This reduction is due to the substrate being covered by a layer of metal film that attenuates the photoelectron signals. Oxidizing the as-deposited sample, it is notable that the chemical shift of the peaks with respect to $SiO_{x<2}$ moves toward higher binding energy. This shift is consistent with the Iwata reported peak shift due to charging phenomenon within a pure SiO_2 and indicates that Si-O-Si bond formation is the dominant reaction during oxidation.[15]

The Hf 4*f* peaks in Fig. 1(b) show that the as-deposited sample has a pronounced asymmetry feature in the XPS lineshape associated with Hf metal (14.41 eV), which is in good agreement with the reported value of 14.40 eV.[16] According to the reported binding energy values for the Hf-Si bond, no evidence (within detection limits) of the Hf-Si bond formation is observed. This lack of Hf-Si bonding is expected, because deleterious Hf-Si bonding will be energetically unfavorable compared to Si-O bonds at the interface. As seen in Fig. 1(b), except for the characteristic peak attributed to Hf-Hf bonds, the resulting broad Hf 4*f* feature contains a significant component associated with the Hf suboxide formed upon deposition. Although the deposition was performed under a high vacuum condition, a small amount of residual oxygen in the chamber likely partially oxidizes the Hf metal film, resulting in higher Hf $4f_{5/2}$ intensity associated with Hf-O bonds. Our observations are similar to those of Watanabe, who reported the partial oxidation of Zr metal film under high vacuum condition.[17] After *in situ* thermal oxidation, the characteristic peak contributed to the Hf metal feature disappears; an apparent Hf doublet (16.9 and 18.9 eV) peak with respect to HfO_2 appears, which is in agreement with that reported by us previously.[18]

Figure 2 demonstrates the transition of XPS spectra for Hf films processed without and with vacuum anneal before *in situ* thermal oxidation. For the sake of comparison, the spectrum from the Si substrate passivated with 1.5 nm chemical SiO_2 (bottom spectrum in Fig. 2) has been displayed. Two peaks are attributed to the following: (1) the Si

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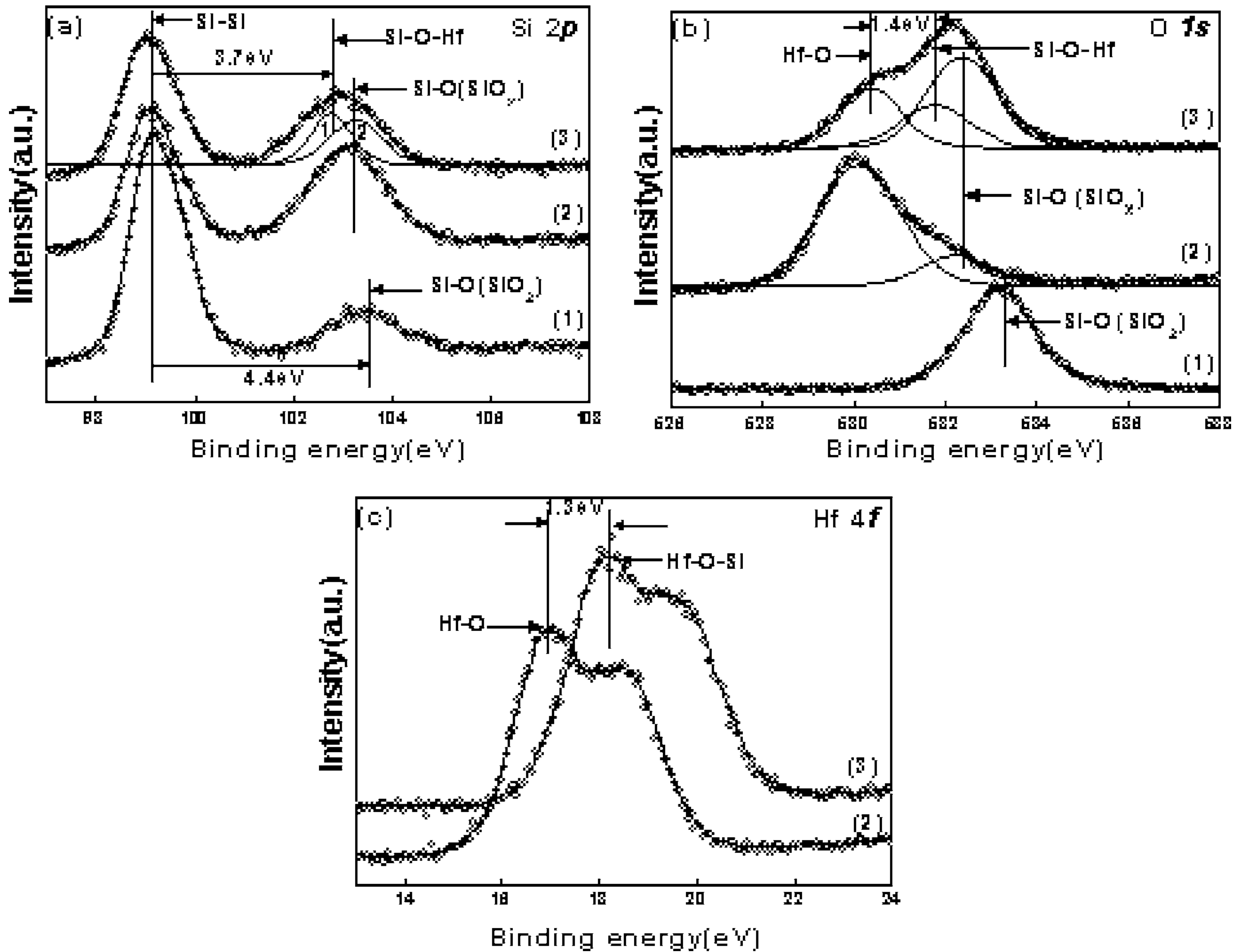

FIG. 2. Core-level XPS spectra of (a) Si 2*p*, (b) O 1*s*, and (c) Hf 4*f* features for the HfO_2/interfacial layer/Si stacks comparing vacuum annealed samples after Hf deposition with unannealed samples. (1) Si with about 1.5 nm chemical SiO_2, (2) as-deposited + *in situ* oxidation, and (3) as-deposited + vacuum annealed + *in situ* oxidation.

substrate at around 99.1 eV; and (2) SiO_2 around 103.5 eV, in agreement with the electron binding energy shift for stoichiometry SiO_2 of 4.4 eV. For the vacuum annealed sample, the deconvoluted spectra of Si 2*p* shows two peaks related to two chemical states. As shown in Fig. 2(a), peak 1, shifted by 3.7 eV relative to the Si substrate, is observed. This lower amount of shift compared to SiO_2 can be assigned to Si-O-Hf bonds formed from interfacial Si^{4+} oxidation states. The paper of Gutowski *et al.* has indicated that $HfSiO_x$ has a bigger binding energy, by a factor of 1.1 eV, compared to the Si 2*p* core-level of SiO_2.[19] According to the paper of Renault *et al.*, the origin of the shift to lower binding energy compared to SiO_2 can arise from the Si second-nearest-neighbor from Si to Hf.[20] Given the small amplitude of the energy shift found for silicate and SiO_2, and the result from Ref. 19, we assign the extra component to Si-rich silicates. Peak 2 in Fig. 2(a), centered at 103.2 eV, results from the contribution of the remnant SiO_x component.

The information of vacuum-annealed-induced silicate formation can also be obtained from the O 1*s* core-level spectra shown in Fig. 2(b). Before deposition, the substrate only presents a peak at 533.3 eV, corresponding to the O 1*s* binding energy of SiO_2. As shown in Fig. 2(b), the deconvoluted spectra of O 1*s* for the vacuum annealed sample displays three subpeaks. One peak at around 530.4 eV is attributed to Hf-O bonds. An additional peak centered at 532.4 eV is attributed to the oxygen bond in the SiO_2 or SiO_x .The binding energy of oxygen bound to the hafnium O 1*s* peak closely matches with its standard location while the binding energy of the oxygen bonded to the Si-O 1*s* peak is 1 eV away from its pure bulk SiO_2 value of 533.3 eV. It has been reported that the binding energy of the O 1*s* photoelectron for the silicate has an intermediate value between the pure metal oxide and SiO_2. Considering the peak shift of +1.4 eV relative to the HfO_2 feature, therefore, the middle peak, centered at 531.8 eV, may be attributed to O in an Hf-O-Si binding configuration. Such a silicate formation has been found to be present at the HfO_2/SiO_2 interface. For the sample without vacuum anneal processing, it is notable that the O 1*s* only greatly results from the contribution of HfO_2 and SiO_x, not Hf-O-Si, which indicates that vacuum anneal-

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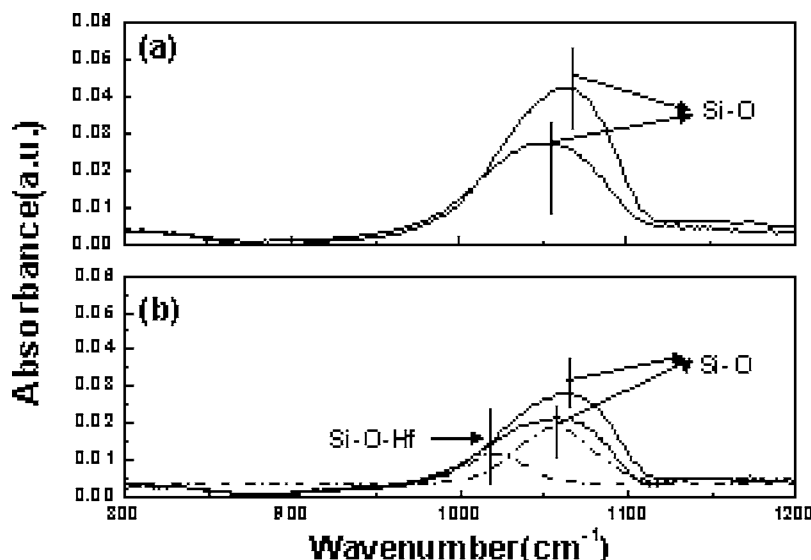

FIG. 3. FTIR spectra for the as-processed samples. The lower spectra in (a) and (b) were taken without and with vacuum annealing after Hf layer deposition. The upper spectra in (a) and (b) show results after post-oxidation annealing at 500 °C in N_2 ambient.

ing accelerates the interface reaction and leads to the formation of silicate.

Many groups have studied the evolution of the binding energy of Si 2*p* and O 1*s* attributed to either the presence of an interfacial silicate layer or by a reduction of the initial SiO_2 surface passivation to produce a suboxide layer. In view of the possibility of these processes taking place, the deconvolution of the binding of metal should be characterized.[21] Figure 2(c) compares XPS data of the Hf 4*f* region for a vacuum annealed sample to that obtained without vacuum anneal after Hf deposition. For the sample without annealing, it is evident that the Hf $4f_{7/2}$ peak at 16.9 eV, separated by 1.3 eV from the Hf $4f_{5/2}$ peak at 18.2 eV, originates from Hf bound to oxygen. However, the Hf $4f_{7/2}$ peak of the vacuum annealed sample shows about a 1.3 eV shift from the unannealed samples (16.9 eV). We contribute the shift to higher binding energy to the formation of Hf-silicate bonding in the vacuum-annealed samples. For example, Wilk *et al.* reported that the binding energy of the Hf 4*f* peak for $Hf_6Si_{29}O_{65}$ is ~1 eV higher than that of HfO_2, about 16.5–17 eV. The peak shift to higher binding energy for Hf-silicate can be caused by the formation of Hf-O bonding in the vicinity of Si.[22]

B. FTIR characterization

In order to confirm the evolution of the interfacial component with and without vacuum anneal processing by XPS, a FTIR analysis of the as-processed sample shows the interfacial layer formation. All the samples obtained were annealed at N_2 ambient at 500 °C for 10 min. As shown in Fig. 3(a), the absorption peak located at 1056 cm^{-1} in the samples without vacuum annealing is due to the Si-O stretching vibration in the interfacial layer. Post-annealing results in the increase of peak intensity and a slight shift toward a higher wave number, which is close to the value of Si-O stretching vibration in bulk SiO_2 at 1075 cm^{-1}. This result indicates that post-annealing can convert suboxide (SiO_x) at the interface into stoichiometric SiO_2, leading to an improvement in the interfacial quality. For the vacuum annealed samples, the characteristic absorbance can be deconvoluted by using two Gaussians centered on 1020 and 1056 cm^{-1}. The peak at 1056 cm^{-1} can be associated with an asymmetrical stretching Si-O-Si mode for SiO_x.[23] According to the conclusion of Rignanese *et al.*, We assigned the peak around 1020 cm^{-1} to the characteristic IR vibration mode for the Hf silicate.[24] The increase of the characteristic absorbance peak intensity corresponds to the increase of thickness. The lower absolute characteristic absorbance after annealing compared with Fig. 3(a) indicates physically less Si-O bonding associated with the structure. As we know, due to the absence of oxygen trapped in the film or the annealing atmosphere, post-deposition annealing will raise the possibility of an interfacial SiO_2 layer. For the vacuum-annealed samples, due to the formation of an interfacial Hf-silicate layer originating from the interfacial reaction, the growth of the interfacial SiO_2 layer resulting from the oxygen diffusion is suppressed, which has been confirmed by Murarka.[25] Therefore, using this method we can design a controllable growth of a high-quality interfacial layer in the formation of high-*k* gate dielectrics.

IV. CONCLUSION

In conclusion, we have investigated the formation of Hf-silicate gate dielectrics by utilizing the solid phase interface between the SiO_2 underlayer and sputtered metallic Hf film. It has been found that the interface reaction is dominated by the formation of an interfacial Si-O-Si bond during *in situ* thermal oxidation of the Hf/SiO_2/Si gate stack at 400 °C. We also find that *in situ* vacuum anneals without air exposure at 700 °C accelerates the interface reaction and results in the formation of a Si-rich Hf-silicate interfacial layer. Characterization by FTIR has demonstrated the vacuum-annealing-induced Hf-silicate interfacial formation and offered compelling evidence that the Hf-silicate interfacial layer is effective against the formation of a SiO_2 layer during post-annealing.

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