High resolution photoemission study of $SiO_x/Si(111)$ interface disruption following *in situ* HfO_2 deposition

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We report on an *in situ* high resolution core level photoemission study of the early stages of interface formation between an ultrathin SiO_x layer (~ 0.3 nm) grown on the atomically clean Si(111) surface and a HfO_2 dielectric layer. Si $2p$ core level spectra acquired at 130 eV photon energy reveal evidence of a chemically shifted component on the lower binding energy side of the substrate peak which is attributed to interface defect states resulting from the incorporation of silicon atoms from the substrate into the interfacial oxide at room temperature. This evidence of Si/SiO_x interface disruption would be expected to increase charge carrier scattering mechanisms in the silicon and contribute to the generally observed mobility degradation in high-k stacks with ultrathin silicon oxide interface layers. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3210794]

Interface formation is a critical aspect relating to the successful incorporation of high-κ dielectric materials, such as HfO_2, into silicon based transistor structures.[1] Electrical characterization studies have shown that the absence of an interfacial silicon oxide layer has a detrimental impact on the carrier mobility in the silicon substrate.[2] Different explanations have been proposed to account for this observed degradation including the coupling of carriers to surface soft-optical phonons[3,4] and remote-Coulomb scattering.[5,6] Both of these mechanisms are reported to have a reduced impact on mobility degradation as the thickness of the SiO_x interlayer is increased however, this negatively impacts on the minimum equivalent oxide thickness (EOT) which can be realized. Controlling the thickness of the interfacial silicon oxide is therefore a prerequisite to achieving EOT values below 1.0 nm which are required for the continued scaling of device geometries. The objective of this experiment was to deposit a high-κ metal oxide onto the thinnest thermally stable silicon oxide grown on the Si (111) surface, in an attempt to preserve the structural integrity of the Si/SiO_2 interface while benefiting from the high-κ value of the HfO_2. The interfacial chemistry of thermal oxide formation on the Si(111) surface is almost identical to that on the technologically important Si(100) surface, differing only in the relative intensities of the individual oxidation states.[7] A number of high resolution photoemission studies[8,9] have interpreted the $SiO_x/Si(111)$ interface as being atomically abrupt which would have associated benefits in terms of interface perfection for device applications.

Soft x-ray synchrotron radiation based photoemission has been used to characterize the formation of the HfO_2 interface with the preoxidised silicon surface by depositing hafnium in an oxygen partial pressure and monitoring the changes in chemistry as the interface is formed. The soft x-ray photoemission experiments were carried out on the SGM1 beamline at the Astrid synchrotron in the University of Aarhus in an ultrahigh vacuum system. The SGM monochromator and the SCIENTA SES-200 electron energy analyzer were set up such that the combined instrumental resolution was 70 meV for the Si $2p$ acquired with 130 eV photons. Prior to dielectric deposition, an ultrathin SiO_2 film was grown on atomically clean boron doped p-type Si(111) of resistivity $1-3$ mΩ cm [$(2-5)\times 10^{19}$ cm^{-3}], which had been cleaned by flash annealing to 1050 °C several times in ultra high vacuum. The oxide was grown in a partial pressure of 5×10^{-7} mbar oxygen at 500 °C for 30 min which resulted in a self-limiting oxide similar to that reported by Morgen *et al.*[10] The HfO_2 layers were subsequently grown by the deposition of hafnium metal from an e-beam evaporator in the same background oxygen partial pressure at room temperature. All core-level spectra have been referenced to the Si $2p_{3/2}$ feature at 99.6 eV and peak attenuation calculations based on the effective escape depth of the electrons from the substrate through an overlayer were used to estimate the HfO_2 thickness.

The change in profile of the Si $2p$ core-level features acquired at 130 eV photon energy as a function of HfO_2 room temperature deposition up to a coverage of approximately 1 nm is shown in Fig. 1. This photon energy corresponds to the maximum surface sensitivity for the Si $2p$ core level, giving experimentally determined electron escape depths of 0.33 and 0.71 nm for Si and SiO_2, respectively.[7] In this figure, the peak intensities have been normalize to the height of the substrate peak so that the relative increase in the oxide signal can clearly be seen. Deposition of HfO_2 on top of the ultrathin interfacial oxide layer should not alter the ratio of Si–O to Si integrated intensities, since both signals should be equally attenuated by the HfO_2 overlayer.[11] The HfO_2 deposition has therefore catalyzed the oxidation at the interface between the silicon substrate and the chemically stable ultra thin thermally grown oxide. This increase in interfacial oxide thickness with high-k deposition has previously been observed in a number of studies[12–14] and has been identified as forming in the initial phase of deposition. The likely cause of this interfacial oxide growth at room temperature is the enhanced dissociation of O_2 into atomic oxygen in the presence of hafnium atoms due to the metal atom catalytic effect.[14] The emergence of a shoulder on the low bind-

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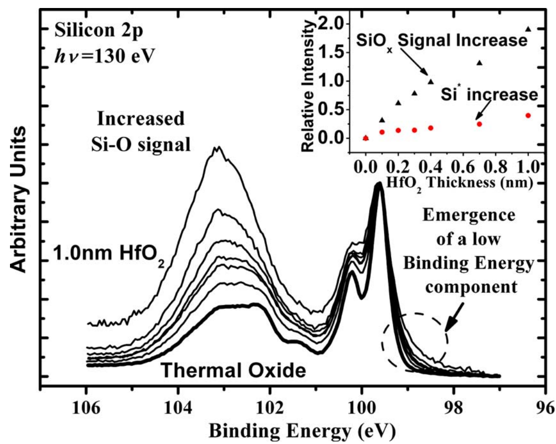

FIG. 1. (Color online) Core level photoemission spectra of the clean silicon surface and following sequential HfO_2 depositions showing an increase in the intensity of the interfacial oxide as the substrate peak intensity is normalized. The inset plots the increase in interfacial oxide thickness and the increase in the intensity of the low binding energy silicon component identified as Si^* in the figure with HfO_2 deposition.

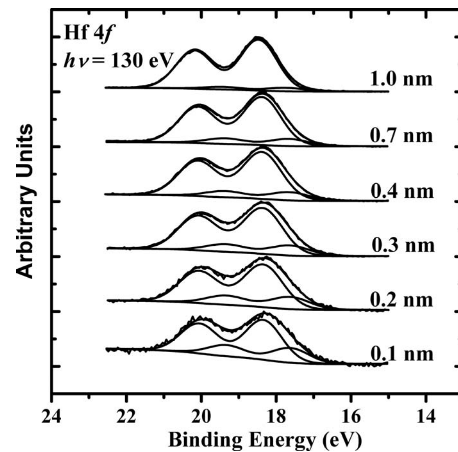

FIG. 3. Normalized photoemission spectra of the Hf 4*f* core level through the deposition sequence showing the suppression of a hafnium suboxide feature as the thickness of the dielectric layer increases.

ing energy side of the silicon substrate peak as the interfacial oxide grows is also apparent in this figure.

These interactions are more clearly observed in the curve fitted spectra in Fig. 2. The surface oxide thermally grown prior to HfO_2 deposition is similar to that reported by Morgen *et al.*[10] and shows evidence of the presence of the four separate oxidation states which are resolved by curve fitting in agreement with previous studies.[7] The thickness of the self limiting oxide was calculated from the ratio of the oxide to substrate integrated intensities to be approximately 0.3 nm which effectively means that it is one monolayer thick, as previously reported by Miyata *et al.*[15] The core-level chemical shift between the Si^{4+} component and that of the silicon substrate signal (ΔBE^{4+}) reduces from 3.54 eV for the ultrathin thermally grown oxide to 3.3 eV after 1 nm of HfO_2 deposition. The change in oxide binding energy with HfO_2 deposition has alternatively been interpreted in terms of the formation of a hafnium silicate interfacial layer[16–18] or the formation of an oxygen deficient substoichiometric interfacial SiO_x layer.[19–21] While it is difficult to definitively determine which of these contrasting explanations more accurately describe the interface chemistry, both agree that the composition differs significantly from homogenous SiO_2. The position of the lower binding energy silicon component at 99.2 eV labeled X in the figure is similar to that observed for the three coordinate rest atoms on atomically clean unpassivated silicon[22] and so could indicate the presence of silicon atoms at the interface without a full complement of four silicon neighbors.[23] For the spectra shown in Fig. 1, the low binding energy silicon component continues to increase in intensity as a function of HfO_2 deposition for the indicated coverage and how this correlates with the observed increase in the silicon-oxygen bond related signal is shown in the inset. While higher coverage of HfO_2 lead to the suppression of the Si 2*p* spectral features, the decrease in signal to noise makes accurate unambiguous spectral analysis impossible. Separate XPS measurements of identically prepared samples indicated a 0.6 nm estimated saturation thickness of the interfacial layer. A number of previous high resolution synchrotron radiation photoemission studies of monolayer terminated Si(111) surfaces have also reported the presence of a chemically shifted silicon component on the lower binding energy side of the substrate peak and attributed this feature to defect states at the surface.[24,25]

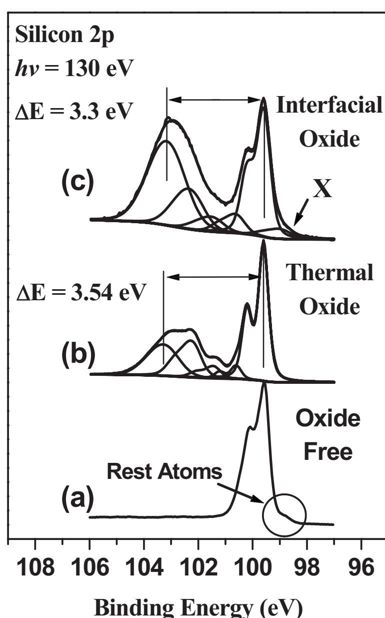

FIG. 2. Curve fitted core level photoemission spectra for (a) the flash cleaned Si surface, (b) the thermally grown ultrathin SiO_x oxide, and (c) an interfacial oxide following HfO_2 deposition with the low binding energy component labeled as X.

Silicon in a hafnium silicide formation would also explain the observation of a low binding energy shoulder on the Si 2*p* core level, as the Hf–Si component has been shown by Carazzolle *et al.*[26] to be shifted −0.45 eV with respect to the substrate peak. The Hf 4*f* core level spectra shown in Fig. 3, acquired at 130 eV photon energy, taken at successive stages during the deposition sequence up to approximately 1 nm coverage, shows two components. The curve fitted lower binding energy component which attenuates with increased deposition is attributed to the formation of Hf suboxides as observed by Xu *et al.*[14] for a similar *in situ* study of room temperature deposition of HfO_2 on atomically clean silicon. The position of the higher binding energy component at 18.35 eV is consistent with stoichiometric HfO_2 and there is no evidence from the Hf 4*f* peak profile of any direct Hf–Si

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bond formation, which results in a chemical shift of approximately 3.1 eV to lower binding energy relative to the fully oxidized hafnium peak.[27] Therefore, the low binding energy shoulder observed in the Si 2*p* spectra cannot be due to Hf–Si formation and is instead attributed to the presence of silicon atoms without a full arrangement of nearest neighbors due to the interface disruption at room temperature.

A similar high resolution photoemission study of interface formation between TiO_2 and an ultrathin oxide on Si(111) reported by Karlsson *et al.*[28] concluded that the atomically abrupt SiO_x/Si interface had been disrupted by the metal oxide deposition. The interfacial oxide which most likely grows in the presence of atomic oxygen by incorporating silicon atoms from the substrate at room temperature does not form the same quality interface with the underlying silicon as SiO_2 thermally grown in an O_2 atmosphere. Instead, a thin disordered region is left at the interface which would be expected to contribute to carrier scattering mechanisms and have a negative impact on carrier mobility at the high-*k* silicon interface. A recent photoemission study of a range of ultrathin dielectric oxides deposited by atomic layer deposition on silicon has linked band bending to the presence of underoxidised and unpassivated silicon at the high-k/SiO_2 interface caused by low temperature deposition.[29] Photoelectron diffraction investigations comparing the structural order at $HfO_2/SiO_x/Si$ interface with the thermally grown SiO_2/Si interface reported evidence of significantly increased disorder.[23]

An initially thicker thermal oxide would be expected to reduce or eliminate the disruption at the Si/SiO_2 interface, however, this would put a limit on the lowest EOT achievable. Therefore, this observed effect of interface disorder would have a similar dependence on the thickness of a SiO_2 buffer layer as the other proposed explanations for mobility degradation.[3–6] While the dielectric constant of the interfacial hafnium silicate layer would be expected to be greater than that of an equivalently thick SiO_2 layer, it would be difficult to compensate for the disrupted nature of the Si/SiO_2 interface. In fact, it could be speculated that the conventional hydrogen based passivation techniques used to improve the electrical characteristics of the thermally formed Si/SiO_2 interface for device application would be less effective in the case of the hafnium silicate—silicon interface because of the induced disorder.

In summary, the extreme surface sensitivity of soft x-ray synchrotron radiation based photoemission has been used to characterize the evolution of interface formation between ultrathin HfO_2 layers and the preoxidised Si(111) surface. Despite the chemical stability of the thin thermally grown silicon oxide layer, the HfO_2 deposition leads to an increase in the thickness of the interfacial oxide which grows by the incorporation of silicon atoms from the substrate. While the saturation thickness of the interfacial layer is estimated to be <0.6 nm, the induced disorder at the Si/SiO_2 interface would be expected to increase carrier scattering mechanisms and hence be a contributing factor to the observed degradation in mobility at high-*k* silicon interfaces. Thicker buffer oxides which could be grown to prevent the interface disruption, thereby preserving the high quality Si/SiO_2 interface, would have a self-defeating effect in terms of the primary objective of reducing the EOT of the dielectric stack. These results would suggest that the search should focus on the identification of high-*k* materials or deposition methods which can prevent the degradation of the Si/SiO_2 interface for ultrathin oxide interlayers in order to preserve its structural integrity while achieving subnanometer EOT targets.

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