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High resolution photoemission study of the thermal stability of the $HfO_2/SiO_x/Si(111)$ system

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ABSTRACT

Synchrotron radiation based photoemission has been used to investigate the thermal stability of HfO_2 dielectric films deposited in-situ on ultra-thin thermally grown silicon oxide. Chemical interactions resulting in the limited formation of hafnium silicide is first detected at 700 °C. Progressively longer anneals at this temperature and subsequently at 800 °C results in the gradual reduction in thickness of the interfacial silicon oxide layer without a corresponding increase in the silicide signal. Annealing at 900 °C results in a complete removal of the interfacial oxide and a substantial increase in the silicide signal. These results suggest that the presence of a thin buffer oxide layer does not completely prevent silicide formation at 700 °C but plays an important role in increasing the decomposition temperature of the hafnium oxide layer to 900 °C.

1. Introduction

A critical aspect relating to the successful incorporation of new high-k materials such as HfO_2, into transistor structures is their thermal stability on silicon substrates at the high processing temperatures typically used for dopant activation in the complementary metal-oxide semiconductor (CMOS) fabrication process. Thermodynamic studies have been undertaken in order to investigate the thermal stability of commonly used binary metal oxides in contact with silicon and have found that either an oxygen excess or deficiency in the dielectric films can promote interfacial reactions [1]. High temperature annealing experiments have been reported by Zeman et al. [2] for TiO_2, ZrO_2 and HfO_2 dielectric layers on a CVD grown buffer oxide on silicon, which was studied by ultra-violet photoemission microscopy and in which they proposed a dielectric decomposition mechanism. The same group [3] reported a more detailed investigation of the $ZrO_2/SiO_2/Si$ system using x-ray photoemission spectroscopy (XPS) to monitor the interface chemistry. In that work the high-κ layers were grown, at room temperature, by e-beam deposition on oxidised silicon and required annealing temperatures in excess of 750 °C to cause significant silicide formation. A more recent study by Schonbohm et al. [4] reported on the thermal stability of ultrathin ZrO_2 films grown by e-beam on the atomically clean silicon surface at room temperature and showed that above 600 °C, there is evidence of $ZrSi_2$ formation. Likewise, for HfO_2 grown at room temperature on a thin (0.5 nm) SiO_2 layer on Si(100), Zeman et al. [2] reported evidence of HfO_2 decomposition at ~1000 °C, while Xu et al. [5] reported that hafnium silicide can be formed by annealing HfO_2 grown directly on atomically clean silicon to 700 °C. The differences in the temperatures at which silicide formation is observed in these studies is likely to be related to whether an interfacial buffer oxide layer is present, as Zeman et al. [2] proposed that silicide formation is delayed until the oxide interlayer is completely consumed.

In this study we use high resolution synchrotron radiation based photoemission spectroscopy to investigate the interface chemistry of thin HfO_2 dielectric films deposited on a thermally grown buffer SiO_2 layer on the Si(111) surface [6] at temperatures up to 1000 °C. The thickness of the interfacial oxide prior to dielectric deposition approximated to a monolayer and as such was the thinnest possible complete buffer oxide layer between the substrate and the HfO_2 layer.

2. Experimental

The soft x-ray photoemission experiments were carried out on the SGM1 beamline at the Astrid synchrotron light source in the University of Aarhus in an ultrahigh vacuum (UHV) system consisting of a preparation chamber (5×10^{-10} mbar) and an analysis chamber (2×10^{-10} mbar). The SCIENTA SES-200 electron energy analyzer collects photoelectrons over a solid angle of 8° centred at 40° from the direction of the incoming photons. The SGM monochromator and the SCIENTA analyzer were set up such that the combined instrumental resolution was 70 meV for the Si 2*p* acquired with 130 eV photons. In order to accurately determine the incident photon energy, core level spectra of Hf 4*f* and Si 2*p* were acquired with both 1st and 2nd order light as the kinetic energy difference gives the precise photon energy. Any variations (typically less than 0.1 eV) were then accounted for

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while plotting the spectra. Silicon spectra were also taken at various photon energies in order to change the effective sampling depth across the interfacial layer as the thickness of the HfO_2 increased. All photoemission scans were taken at normal emission with respect to the sample position. Prior to dielectric deposition, an ultra thin SiO_2 film was grown on atomically clean boron doped p-type Si(111) of resistivity 1–3 mΩ-cm ($2–5\times10^{19}$ cm^{-3}) which had been cleaned by flash annealing to 1050 °C several times in ultra high vacuum. A self limiting SiO_2 layer was grown on Si(111) in ultra high vacuum in an oxygen partial pressure of 5×10^{-7} mbar for 30 min at 500 °C in a similar way as reported by Morgen et al. [6]. The HfO_2 layer was subsequently grown by the deposition of hafnium metal from an e-beam evaporator in the same background oxygen partial pressure at a substrate temperature of ~250 °C. The substrate was heated during depositions by direct current heating of the low resistivity silicon substrate with the temperature having been calibrated by attaching a thermocouple to a similarly sized sample. For the high temperature vacuum anneals, the sample temperature was recorded by an infrared pyrometer.

3. Results

Fig. 1 shows the silicon 2*p* core level profile acquired at 130 eV photon energy for the *in-situ* grown surface oxide, prior to hafnium deposition and is in agreement with previous studies [7]. This photon energy is chosen as it has been shown to have the highest surface sensitivity for the Si 2*p* core level with an effective sampling depth of approximately 2 nm [8]. The spectrum is similar to that previously reported [9] and shows clear evidence of the presence of the four separate oxidation states, Si^{1+}, Si^{2+}, Si^{3+} and Si^{4+} corresponding to Si_2O, SiO, Si_2O_3 and SiO_2 which are resolved by curve fitting [7]. The thickness of the self limiting oxide was calculated to be approximately 0.3 nm which effectively means that it is one monolayer thick in agreement with the studies of Miyata et al. [10]. The figure also shows the profile of the core level following the deposition of sufficient HfO_2 to almost completely suppress the substrate signal which would correspond to the coverage of approximately 2 nm. The change in the relative intensity of the oxide and substrate components has previously been interpreted in terms of an increase in the thickness of the interfacial oxide layer as the dielectric is deposited [7]. The observed broadening of the Si 2p peak on the low binding energy side was previously detected following the deposition of HfO_2 on an ultrathin interfacial thermal oxide and was attributed to the presence of silicon atoms without a full arrangement of nearest neighbours due to the interface disruption (HfO_2 induced oxidation of silicon) at low temperature [7]. Si 2*p* core-level spectra after sequential 30 s high temperature anneals between 600 °C and 1000 °C in steps of 100 °C are displayed in Fig. 2. Up to 600 °C, there is no discernable change to the peak profile indicating the stability of the film up to this temperature. For the first 30 s anneal at 700 °C anneal, the relative change in the intensities of the oxide and substrate peak is interpreted as a reduction in the thickness of the interfacial silicon oxide layer, as there is no significant change in the intensity or the peak position of the hafnium oxide signal. There is also a broadening observed in the Si 2*p* feature when compared with the substrate signal in Fig. 1 which reflects the disordered nature of the silicon bonding at the interface [11,12]. The subsequent anneals at 700 °C for longer periods result in the progressive reduction in the intensity of the oxidised silicon component relative to the substrate signal reflecting a decrease in the thickness of the interfacial oxide. At 800 °C there is only a small interfacial oxide component remaining which is completely removed by the 900 °C anneal. The final anneal at 1000 °C has no significant additional impact on the profile of the Si *2p* core level which has now a well defined substrate component peak and a silicide component at lower binding energy. The binding energy of the as deposited Hf 4*f* spin–orbit–split component peaks acquired at a photon energy of 47 eV shown in Fig. 3 is consistent with a fully oxidised HfO_2 film composition [13]. The first clear sign of a Hf–Si bonding signal is seen at an annealing temperature of 700 °C with the appearance of Hf silicide 4f 5/2 and 7/2 signals at 14.6 eV and 16.3 eV, respectively [11,12]. The detection of this silicide feature is consistent with the low binding energy shoulder on the Si 2*p* bulk feature. There is a significant increase in the intensity of the Hf–Si bonding features at 900 °C and a complete disappearance of the Hf–O bonding signal following annealing at 1000 °C. Separate XPS studies undertaken for the same annealing cycles revealed that there was no evidence of a change in the stoichiometry of the HfO_2 film prior to its eventual decomposition to form hafnium silicide.

The valence band spectra as function of thermal annealing also shown in Fig. 4 indicate that up to a temperature of 800 °C there is little change in the valence band features attributed to HfO_2 [14,15]. However, above this temperature there is a clear increase in the signal between 0 eV and 4 eV binding energy. This is consistent with the observations from the Hf 4*f* and Si 2*p* spectra at these temperatures which indicate the formation of a metal silicide at the surface. The impact of increasing the thermal annealing time at 700 °C on the Hf 4*f* profile is shown in Fig. 5 to have no noticeable effect on the Hf–Si bond concentration, with the Hf-Si signal remaining at $5\pm1\%$ of the total Hf 4*f*

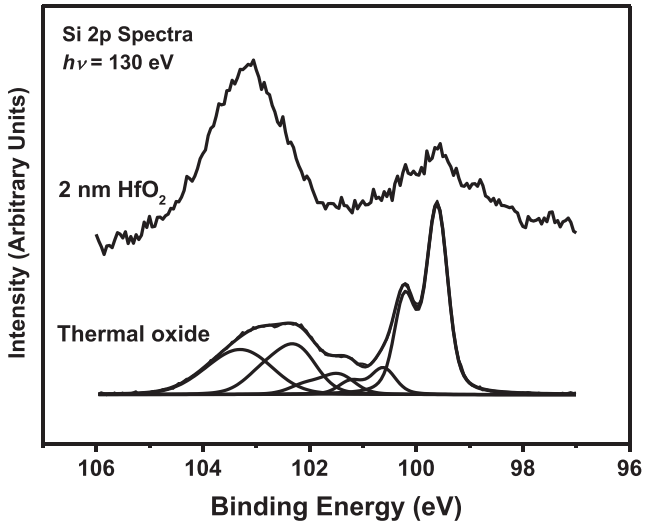

Fig. 1. Silicon 2p core level photoemission spectra of the curve fitted thermally grown ultra thin oxide and following deposition of approximately 2 nm HfO_2.

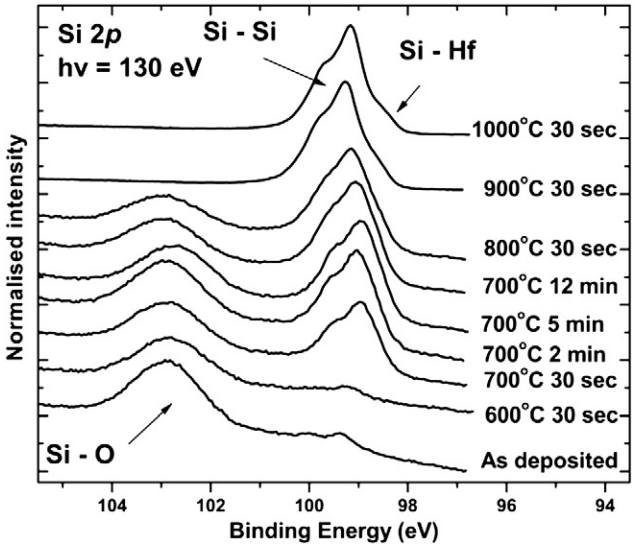

Fig. 2. Changes induced in the profile of the Si 2p core level at a range of annealing temperatures and times.