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To cite this article: B Brennan et al 2008 J. Phys.: Conf. Ser. 100 042047

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Photoemission studies of the interface formation of ultrathin MgO dielectric layers on the oxidised Si(111) surface

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Magnesium oxide (MgO) has been proposed as a medium-k dielectric material for integration into advanced transistor fabrication. In this study, soft x-ray synchrotron radiation based photoemission and conventional x-ray photoelectron spectroscopy have been used to characterise the evolution of the MgO/Si(111) interface as an ultrathin film is been grown. The MgO film was grown by thermally depositing magnesium in an oxygen partial pressure at room temperature. The Mg2p peak profile indicates that the magnesium exists in a single chemical state throughout the deposition sequence with a binding energy indicative of MgO. The initial submonolayer deposition resulted in the Si2p peak shifting 0.3eV towards higher binding energy consistent with electron transfer between the deposited magnesium and the substrate. This is accompanied by an increase in the intensity of the Si oxidation states indicating growth of the interfacial oxide thickness. As the MgO film thickness increases, the Fermi level moves back to within 0.1eV of its original midgap position. Subsequent XPS measurements show that the saturation thickness of the interfacial silicon oxide layer is less than 0.7nm. The valence band offset has been measured and the conduction band offset has been deduced by estimating the bandgap of the thin dielectric film. The valence band offset between the thin MgO layer and the silicon substrate is 4.1eV. The MgO workfunction was 2.8eV and assuming an electron affinity value of 0.85eV, the bandgap of this film is 6.72eV, smaller than that reported for bulk MgO. The calculated conduction band offset is 1.5eV which should be a sufficiently high barrier to minimise leakage currents.

1. Introduction

With the continued scaling of the gate dielectric in transistors, silicon dioxide is reaching a fundamental limit to its performance, with thinner layers allowing for an unacceptably high leakage current. It is therefore necessary to look at and investigate the use of alternative materials to replace it for future devices. Thicker layers with a higher dielectric constant ($\kappa$) will allow for an equivalent SiO$_2$ thickness with a lower leakage current. Already, hafnium dioxide (HfO$_2$) is being to be used as an alternative material for this purpose [1] but there is still room for further development in this area. The objective of this study was to investigate the interface formation between a magnesium oxide overlayer and an ultrathin silicon dioxide layer grown on the atomically clean p-type Si(111) surface in ultra high vacuum. While having a dielectric constant only twice that of silicon dioxide, MgO is chemically very stable and should reduce chemical reactivity at the silicon surface. Bulk MgO has a bandgap of 7.3eV which has the potential to ensure band offsets of sufficient magnitude to minimise leakage currents.
2. Experimental

The soft x-ray photoemission experiments were carried out on the SGM1 beamline in Astrid at the University of Aarhus in an ultrahigh vacuum (UHV) system consisting of a preparation chamber (6x10^{-10} mBar) and an analysis chamber (3x10^{-10} mBar). The SCIENTA SES-200 electron energy analyzer which 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 70meV for the Si 2p acquired with 130 eV photons. All photoemission scans unless stated were taken at the NE 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 m\(\Omega\)-cm (2-5 \times 10^{19} cm^{-3}) which had been cleansed by flash annealing to 1050°C several times in ultra high vacuum. The oxide was grown in a partial pressure of 5 x 10^{-7} mbar oxygen at 500°C which resulted in a self limiting oxide thickness of the order of 0.7 nm similar to the procedure reported by Morgen et al [2]. The magnesium metal was evaporated from a resistively heated tantalum pouch which contained high purity magnesium chips in a stepwise incremental fashion in an oxygen partial pressure of 5 x 10^{-7} mbar in a procedure similar to that described by Xu et al [3]. The ionization potential (IP) of the samples during the dielectric growth was determined by subtracting the width of the electron distribution curve (EDC) from the photon energy. Conventional x-ray photoelectron spectroscopy was carried out using an Mg k\(\alpha\) (h\(\nu\) = 1253.6 eV) x-ray source with a pass energy of 20eV. Oxygen 1s, magnesium 2s and 2p, carbon 1s and silicon 2p peaks were scanned along with a survey scan from 0 – 600 eV. Atomic Force microscopy was carried out with a Digital Instruments Nanoscope III-a in contact tapping mode at room temperature.

3. Results

As the Si is oxidised, the four possible oxidation states can be detected due to the ultra thin nature of the layer, high resolving power of the spectrometer and surface sensitivity resulting from using a photon energy of 130eV. The 4\(^{+}\) oxidation state makes up the bulk for SiO$_2$. The 1\(^{+}\) and 2\(^{+}\) states are interface localised whereas the 3\(^{+}\) states are found predominantly at the surface which is why its signal shows the highest intensity at an ultrathin thickness as seen in ‘figure 1’ [2].

![Figure 1](image1.png)

**Figure 1.** Scan of Si 2p peak with ultrathin SiO$_2$ (<0.7 nm) grown in O$_2$ at 500°C.

![Figure 2](image2.png)

**Figure 2.** Si 2p spectra at a photon energy of 130eV showing the suppression of Si peak and increase in SiO$_2$ with sequential MgO deposition.

As the MgO is deposited, the Si peak shifts by 0.3eV to a higher binding energy and this is also accompanied by deterioration in the definition of the Si oxidation states as seen in ‘figure 2’. This is

![Figure 3](image3.png)

**Figure 3.** Sequential Mg 2p spectra at a photon energy of 79 eV showing MgO in a single chemical state as deposition time increases.
consistent with electron transfer to the substrate as Mg acts as an electron donor. The thickness of the grown interfacial oxide saturates at less than 0.7nm. ‘Figure 3’ illustrates that the position of the Mg 2p peak does not change throughout the deposition sequence suggesting that the MgO is going down in a single chemical state, with a binding energy indicative of MgO.

**Figure 4.** Work function and valence band spectra after MgO deposition showing a valence band offset of 4.1 eV and a workfunction of 2.8 eV.

From valence band measurements shown in ‘figure 4’, the valence band offset between the oxide and the silicon substrate was seen to decrease by 0.3ev from 4.4eV for SiO\textsubscript{2} to 4.1eV for MgO. The work function of the thickest film was 2.8eV. When this is used in conjunction with the energy position of the valence band maximum it is possible to construct an interfacial energy level diagram as illustrated in ‘figure 5’ which shows that the ionization potential for this film is 7.57eV, giving a bandgap of 6.72 eV, smaller than values for bulk MgO but sufficient to inhibit charge carrier transport across the gap.

**Figure 5.** Energy band diagram for MgO deposited on an ultrathin SiO\textsubscript{2} interfacial layer.

**Figure 6.** XPS spectra of the Mg 2s, Si 2p and O 1s peaks. At 700°C an increase in the SiO\textsubscript{2} peak is seen as the Mg peak decreases.
For conventional XPS measurements, samples were prepared in the same way as before but with a thicker layer of MgO deposited due to the greater sampling depth of the Mg $k\alpha$ x-rays compared to the soft x-ray synchrotron radiation. The samples were then annealed in vacuum for 10 minutes at various temperatures from 600°C to 900°C. The film remains stoichiometric up to 700°C above which the MgO decomposes with the oxygen reacting with the silicon to form SiO$_2$ and the Mg desorbing from the surface. ‘Figure 6’ shows the increase in the SiO$_2$ peak along with a decrease in the Mg 2s peak as the annealing temperature increases above 700°C. In the O 1s spectra, there is an increase in the intensity of a higher binding energy feature which begins to dominate above 800°C resulting in a peak shift as the temperature increases, consistent with an oxygen transfer from MgO to SiO$_2$.

![AFM images of MgO on silicon (111) surface showing island growth.](image)

**Figure 7.** AFM images of a 2x2 µm area of MgO on silicon (111) surface showing island growth.

AFM images in ‘figure 7’ clearly show island growth with an RMS roughness of 5.33 nm and an average height of 11.6 nm for a sample with approximately 1.5 nm of MgO from XPS thickness analysis. This deposition was carried out at room temperature which could account for the highly non-uniform nature of the deposited layer. Experiments are ongoing to investigate film topography for MgO layers deposited on surfaces at elevated temperatures.

4. Conclusions
MgO has been deposited on Si(111) surfaces with an interfacial SiO$_2$ buffer layer and growth monitored using synchrotron based photoemission. The MgO films grown had bulk-like chemical composition and there was an initial electron transfer between the MgO and SiO$_2$ layer. There was an increase in the intensity of the interfacial oxide layer which saturated at a thickness of approximately 0.7 nm. Valence and conduction band measurements were taken which allowed a band gap of 6.72 eV to be calculated which is sufficiently high to minimize leakage current across the gap.

Annealing the sample showed the MgO layer to be stable up to 600°C above which the magnesium desorbed from the surface and an increase was seen in the SiO$_2$ peak. AFM images also showed island growth of MgO on the surface with large surface roughness.

References

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