Growth and Characterisation of Thin MgO Layers on Si(100) surfaces

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In this study, the growth, stochiometry and electrical characteristics of MgO thin films, deposited by electron beam evaporation on Si(100) surfaces, have been investigated. Films of different thicknesses were deposited on HF last and chemical oxide Si(100) surfaces in order to determine the effect of factors such as film thickness, surface preparation and substrate temperature on film growth. Using atomic force microscopy (AFM), the predominant film growth mechanism was found to be Volmer Weber, with factors such as film thickness determining the height at which 3 dimensional islands coalesce to form a continuous film. Chemical analysis using X-ray photoelectron spectroscopy (XPS) showed that MgO deposition on hydrogen terminated silicon surfaces produced films of more uniform thickness than those deposited on surfaces with a native chemical oxide. XPS spectra of the O1s core level exhibits two oxygen peaks, a lower binding energy peak (LBE) which can be attributed to the lattice oxygen in the MgO, along with a higher binding energy (HBE) oxygen peak associated with the formation of magnesium hydroxide at the surface of the MgO film upon air exposure. Increasing the substrate temperature during deposition was shown to improve the stochiometry of the films. Based on electrical characterisation of Pd/MgO/Si(100) capacitor structures, the dielectric constant of the MgO layer is calculated as 8.1.
1. Introduction
Magnesium oxide has been suggested as a potential candidate to replace SiO$_2$ as the gate oxide layer in advanced transistor fabrication. MgO has a dielectric constant more than twice that of SiO$_2$ and a bulk bandgap of 7.3eV. The capability of MgO as a future replacement of SiO$_2$ is apparent in recent work to integrate MgO with silicon and high mobility III-V substrates [1-4].

Yan et al. [4] have recently reported on MgO films sputter deposited from a magnesium target on silicon substrates in an oxygen ambient. Sharp interfaces with interface densities at the MgO/Si interface comparable to that of the conventional SiO$_2$/Si system following annealing in forming gas (0.9N$_2$/0.1H$_2$) at 450 °C were presented.

This paper reports the chemical, micro structural and electrical properties of MgO thin films deposited on Si(100) substrates using electron beam evaporation from MgO pellets. The effect of the Si(100) substrate preparation prior to MgO deposition (HF last or chemical oxide) is also presented.

2. Experimental Procedure
Hydrogen terminated silicon surfaces were prepared by dipping n and p type (100) Si wafers (10$^{15}$ cm$^{-3}$) in a solution of 5% hydrofluoric acid (HF) for 1 minute. They were dried using nitrogen gas and immediately inserted into the deposition system. MgO films were deposited on the substrates using electron beam evaporation of MgO pellets of 99.9% purity, at a deposition rate of 0.1 Å/s in an O$_2$ ambient. Following evaporation, chemical analysis was carried out using XPS in a separate system. The samples were exposed to ambient conditions for approximately 5 minutes prior to XPS characterisation. Metal Oxide Semiconductor (MOS) structures were also fabricated by depositing 100 nm of Pd onto the MgO surface using a lift off process. The electrical measurements on the Si(100)/MgO/Pd structures were performed in a microchamber controlled environment (Cascade Microtech Summit 12000 Theta) using a HP4156A and a HP4284A for IV and CV analysis. Measurements were performed at 25°C.

3. Results
The XPS spectrum of an e-beam deposited MgO film (12nm) in Figure 1 (a) shows the presence of two oxygen peaks in the O 1s core level, similar to that reported by Corneille et al [5]. The lower binding energy (LBE) peak was attributed to the lattice oxygen in the MgO. This is in agreement with reference spectra recorded in the same system from a single crystal magnesium oxide sample. The HBE peak can be seen in both the O 1s spectrum in Figure 1 (a) and in the Mg 2p spectrum in Figure 1 (b). Off normal photoemission scans showed that the higher binding energy (HBE) peaks were surface localised.

![Fig. 1. XPS spectra of 12nm MgO (a) O 1s and (b) Mg 2p show the presence of a surface hydroxide after ambient exposure of ~ 1 minute.](image-url)
Exposure to ambient conditions caused the HBE peaks to grow rapidly, as shown for the O1s in Figure 2 (a). This rapid growth suggests that the peaks are due to the formation of magnesium hydroxide, Mg(OH)$_2$, on the surface of the film. A linear relationship exists between the growth in intensity of the magnesium and oxygen higher binding energy peaks following air exposure, which suggests that they are both related to the formation of the surface hydroxide species. As this Mg(OH)$_2$ layer is surface localized, it is reasonable to assume that intensity of the related spectral features should scale with the surface area of the film, which is directly correlated with the flatness of the deposited film. It was therefore possible to use the ratio of the two oxygen peaks as a measure of film surface area and, as such, the flatness of the film. Using this ratio, the effect which factors such as substrate preparation and temperature have upon film uniformity was determined.

Annealing samples exposed to air for 7 days for 1 minute at 500°C in Argon reduced the surface hydroxide peak, shown in Figure 2 (a), and greatly improves the stochiometry of the films, which were predominantly 20% oxygen deficient for room temperature depositions but showed an oxygen to magnesium ratio of 1:1 after anneal. XPS studies show that heating the substrate during the deposition reduces the HBE oxygen peak, illustrated in Figure 2 (b), which is consistent with a flatter more uniform film. Stochiometry calculations based on XPS spectra also show that samples deposited at higher substrate temperatures have magnesium to oxygen ratio approaching 1:1.

Fig. 2. (a) The growth of the HBE O 1s component with air exposure and the effect of a subsequent anneal. This spectrum was taken from a 12nm MgO. (b) XPS spectra indicating that depositing MgO at elevated substrate temperatures produces flatter, more continuous films reflected in the reduced intensity of the O1s HBE component.

MgO films grown on hydrogen terminated silicon surfaces were flatter and more continuous than those grown upon the silicon native oxide. Films grown after HF passivation also show on average 10% less oxygen deficient than those grown on the silicon native oxide.

AFM results taken from films of various thicknesses show the presence of MgO islands with an average height of ≈ 2 nm and RMS roughness of 0.5 nm. These roughness values are in close agreement with those reported by Kim et al [6] for 100 nm thick MgO films. The presence of islands, which coalesce to form a more continuous film, is indicative of Volmer Weber growth for room temperature deposition. This result is supported by XPS measurements (not shown), and suggest that island surface area reduces as the film thickness increases.

XPS spectra shown in Figure 3 (a) taken from 5nm films deposited on hydrogen terminated Si show little evidence of an interfacial oxide. The IV and CV characteristics of the n-type Si(100)/MgO/Pd structures (CV at 100 kHz) for a nominal 20nm MgO films are shown in Figure 3 (b). From the maximum accumulation capacitance on the HF last terminated Si(100) surface, and
assuming no interface oxide is present for the 20nm MgO structure, the dielectric constant of MgO was calculated as 8.1. This is close to its theoretical value. Figure 3 (b) also indicates the reproducibility of the CV response. The presence of interface states can be seen on the CV curve, however this is to be expected for high-

$k$ films deposited at room temperature without subsequent annealing in $N_2$ or $H_2/N_2$ [7].

Fig. 3. (a) XPS spectra taken 5nm films show little evidence of a Si interfacial oxide (b) C-V (and inset IV) characteristics at 100 kHz for 20 nm MgO film on n-type Si(100)

4. Conclusions
The dominant growth mechanism for electron beam deposited MgO on Si at room temperature is Volmer Weber growth. The flatness and uniformity of the MgO films can be improved by depositing at elevated temperatures. Exposing MgO thin films to ambient conditions causes the rapid growth of magnesium hydroxide on the surface layer of the film. MgO films deposited at room temperature are predominately oxygen deficient, this can be addressed by depositing at higher substrate temperatures or by depositing films in an oxygen background pressure. XPS analysis indicates little evidence of an SiO$_x$ layer between the Si(100) substrate and the MgO film. Electrical measurements based on Si(100)/MgO/Pd structures exhibit conventional high frequency CV behavior. The dielectric constant of MgO is calculated as 8.1.

Acknowledgements
The authors thank Mr. Dan O’Connell and Ms. Mary White, Tyndall National Institute for sample processing. The authors would like to acknowledge the following for financial support of this work: Science Foundation Ireland for the National Access Program (NAP) at the Tyndall National Institute; Irish Research Council for Science, Engineering and Technology; Intel Ireland. The authors would also like to thank Dr. Paul Hurley, Rathnait Long and Eamon O’Connor for electrical characterisation and discussion.

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