Analysis of hafnium containing powders and thin films for CMOS device applications

C M McGilvery\textsuperscript{1,2}, D W McComb\textsuperscript{1,z}, M MacKenzie\textsuperscript{2}, A J Craven\textsuperscript{2}, S McFadzean\textsuperscript{2} and S De Gendt\textsuperscript{3}

\textsuperscript{1} Dept. of Materials and London Centre for Nanotechnology, Imperial College London, London, SW7 2AZ, UK
\textsuperscript{2} Dept. of Physics and Astronomy, University of Glasgow, Glasgow, G12 8QQ, UK
\textsuperscript{3} IMEC, Kapeldreef 75, B-3001 Leuven, Belgium, also at Department of Chemistry, KU Leuven, B-3001 Leuven, Belgium

\textsuperscript{z} email: d.mccomb@imperial.ac.uk

Abstract. As the SiO\textsubscript{2} or Si(O,N) layer in complementary metal oxide semiconductor (CMOS) devices reaches its atomic limits it is necessary to find suitable materials that will allow further device scaling. Leading candidate materials include hafnia and hafnium silicate; however, issues remain regarding their stability which must be resolved. This paper highlights some of these issues in hafnium-containing gate stacks. Hafnium silicate bulk powders were investigated to gain a better understanding of the chemistry and crystallisation processes involved. This was done using x-ray diffraction, thermal analysis, transmission electron microscopy and electron energy-loss spectroscopy.

1. Introduction
It has become increasingly necessary to find a replacement for amorphous SiO\textsubscript{2} and Si(O,N) in silicon based metal oxide semiconductor field effect transistors (MOSFETs). An ideal replacement material would have a high dielectric constant (\(\kappa\)), and have good stability after high temperature activation at 1000°C. Although hafnia (HfO\textsubscript{2}) and hafnium silicate ((HfO\textsubscript{2})\textsubscript{x}(SiO\textsubscript{2})\textsubscript{1-x}, also referred to as ‘HfSiO’) are currently leading candidates as high-\(\kappa\) replacement materials, many issues remain. Here we consider these two materials and present results highlighting some of the continuing stability issues.

2. Experimental and Discussion
Fig 1 shows a typical Si/SiO\textsubscript{2}/HfSiO/TiN/poly-Si gate stack prepared by researchers at IMEC in Belgium. In this case a 4nm layer of (HfO\textsubscript{2})\textsubscript{0.7}(SiO\textsubscript{2})\textsubscript{0.3} has been deposited. The wafer has reached a maximum temperature of 1000°C for 10s as the final activation anneal. Due to the thermal budgets during processing, issues remain regarding crystallisation, stability, diffusion, interface roughness and interfacial reactions. In this paper we consider issues relating to the crystallisation and phase separation of the layers, and interfacial reaction products. You will note from Fig 1 that at the lower silicon/high-\(\kappa\) interface the SiO\textsubscript{2} layer is wider than the \(\sim\)1nm SiO\textsubscript{2} layer grown as part of the process [1]. This layer is thought to have grown due to diffusion of oxygen from the high-\(\kappa\) layer to the silicon substrate. (Growth of the SiO\textsubscript{2} layer can also be caused by electron beam induced phase separation [2] adding extra difficulty to data interpretation.) Interfacial reactions also occur at each of the
interfaces in the gate stack. Interface reactions and growth of the SiO\textsubscript{2} lower the overall performance of the gate stack.

![Figure 1](image_url): Example of typical complementary metal gate oxide (CMOS) gate stack: Si/SiO\textsubscript{2}/(HfO\textsubscript{2})\textsubscript{0.7}(SiO\textsubscript{2})\textsubscript{0.3}/TiN/poly-Si

Deposition: 1nm SiO\textsubscript{2}, 4nm HfSiO, 10nm TiN

While we want the high-\(\kappa\) dielectric layer to remain amorphous, under high temperature processing conditions the layer often partially or fully crystallises. In Fig 1 a small degree of phase separation may have occurred along the length of the HfSiO layer. By increasing the relative amount of silica in the layer, it is possible to inhibit crystallisation and phase segregation. However, in the case of an ‘HfSiO’ layer, even if crystallisation does not take place, separation into amorphous hafnia and silica rich regions occurs. The width of the layer can affect the amorphous-crystalline phase transformation and the crystalline phase that forms. We have investigated gate stacks with poly-Si capping layers and HfSiO layer widths of 4 and 20nm. The 4nm layers do not show the same degree of crystallisation or phase separation as the 20nm layers do. This may be due to the increased strain caused by the gate material on the thinner layers. Triyoso et al. [3] note that the presence of the gate on top of a 20nm HfO\textsubscript{2} layer (after a 1000°C anneal), relative to uncapped wafers (after annealing to 900°C), changes the crystallisation phase from monoclinic hafnia (m-HfO\textsubscript{2}) to a mixture of m-HfO\textsubscript{2} and tetragonal hafnia (t-HfO\textsubscript{2}). Reducing the deposition temperature of the hafnia layer also increased the t-HfO\textsubscript{2} content after annealing. This is most likely due to the mechanical constraint of the gate material, inhibiting the volume expansion necessary for the m-HfO\textsubscript{2} phase to form. Crystallisation within the high-\(\kappa\) layer results in grain boundaries which provide a path for leakage current across the gate leading to device breakdown. We need to be careful when interpreting TEM images of the HfSiO layer as the electron beam can induce crystallisation of the layers and silica layer width growth (see below) [2].

To try to understand further the mechanism of crystallisation and phase separation in the high-\(\kappa\) layer, bulk HfSiO powders were prepared and investigated using thermal analysis, x-ray diffraction (XRD), transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS). Although the reactions that take place in the bulk are far from the thin film situation, it is vital to have a clear understanding of the crystallisation processes occurring here, before the thin films can be fully understood. Stoichiometric HfO\textsubscript{2} and HfO\textsubscript{2}-SiO\textsubscript{2} powders were prepared from a hafnium oxychloride and butoxide precursors. Two key XRD experiments were carried out on the different powders. Firstly a sample was heated in-situ in an X'Pert PRO Panalytical high temperature instrument fitted with an Anton Paar XRK-900 environmental heater and heated from 300-900°C, with a heating rate of 60°C/min, taking scans every 20°C. (This work was carried out at the Center for Nanoscale Materials Sciences (CNMS) at Oakridge National Laboratory (ORNL), USA). This revealed that crystallisation occurred at about 460°C into the m-HfO\textsubscript{2} phase, the expected stable room temperature phase. There was a small peak associated with the t-HfO\textsubscript{2} phase but this disappeared by 520°C. Only m-HfO\textsubscript{2} was present up to 900°C. To investigate the effects at higher temperatures, samples were heated in a
furnace for 24 hours to 800, 1000 and 1400°C and for 12 hours to 1700°C. These were then analysed at room temperature on a Philips PW1700 series automated powder diffractometer using Cu Kα radiation. The results for the oxychloride prepared powders are reproduced from ref [4], and displayed in Fig 2.

Figure 2: Ambient XRD of HfO$_2$-SiO$_2$ oxychloride powders after heating to temperature for 24 hours (12 hours for 1700°C) [4]

In Fig 2 we see the t-HfO$_2$ phase appear by 1400°C but disappear again by 1700°C. This is slightly surprising as according to the HfO$_2$-SiO$_2$ phase diagram, and by extrapolation from the more complete ZrO$_2$-SiO$_2$ phase diagram, the tetragonal phase should only be present above 1750°C. Stabilisation of the tetragonal phase of zirconia at low temperatures has been attributed to a number of causes such as a critical size effect first proposed by Garvie [5], surface stabilisation energy, incorporation of impurities onto the surface or the lattice itself and oxygen vacancies [6]. As already mentioned, we know that silica stabilises the amorphous phase in thin films. Here, the silica causes the t-HfO$_2$ phase to stabilise at temperatures lower than would be expected in a silica free system. Silica also crystallises by 1400°C in the form of cristobalite (c-SiO$_2$) and then combines with m-HfO$_2$, t-HfO$_2$ and any remaining amorphous material to form HfSiO$_4$ by 1700°C. Fig 3 contains some TEM images of a sample heated to 1400°C. We expect this sample to contain silica, m-HfO$_2$ and t-HfO$_2$ particles. These images illustrate some of the complexities of the system we are studying. We get a number of large (>50nm) particles which are thought to be m-HfO$_2$, surrounded by amorphous material. On closer inspection of the amorphous region it is observed that there are many randomly spaced spherical particles 2-10nm in size. It is thought that these are t-HfO$_2$ which nucleate at this temperature from remaining hafnia in the amorphous matrix. This is deduced by comparing the particle sizes from XRD with TEM images. The presence of the silica rich matrix induces a strain on the particles, not allowing them to grow beyond a certain size and hence stabilising them until they are consumed to form HfSiO$_4$.

By probing the near-edge structure (ELNES) in EELS, detailed information on the chemistry, structure and bonding of the local atomic environment can be gained. This in turn provides us with information regarding the crystallisation process occurring as the amorphous powders are heated. Oxygen K-edge data obtained from the butoxide prepared powders is shown in Fig. 4. Fig 4(a) was recorded from a sample prepared from the butoxide precursor containing only monoclinic and amorphous HfO$_2$. The remainder of the edges in Fig 4 were taken from HfO$_2$-SiO$_2$ butoxide powders.
after calcination at 1700°C. The spectra labelled (a), (b) and (c) in Fig 4 are in excellent agreement with published data for m-HfO$_2$, HfSiO$_4$ and a-SiO$_x$, respectively [2].

The remaining edges, (d)-(g), exhibit fine structure that at this stage we cannot attribute to a known phase. Either new phases may have formed or we may have an overlap of two or more edge shapes - many of the particles are surrounded by a thin layer of amorphous material. Standards from these powders and from the literature have been obtained for all of the main materials being investigated apart from t-HfO$_2$ which, to the authors’ knowledge, is not present in the literature. Because the t-HfO$_2$ crystals are small (2-7nm) and are often surrounded by amorphous material this is proving to be difficult.

The standards obtained from the powders are vital to help with interpretation of the crystallisation in the high-κ layer and interfacial reaction products at the interfaces in the gate stacks.

![Figure 4: EELS O K edges taken from sol-gel powders. (a) m-HfO$_2$, (b) HfSiO$_4$, (c) a-SiO$_x$, (d)-(g) show edges obtained from powders containing crystalline silica, hafnia, hafnium silicate and amorphous material](image)

3.0 Conclusions

We have highlighted some of the problems associated with the incorporation of new high-κ materials into MOSFETs, and have considered hafnia and hafnium silicate in particular. We have discussed the need to have a good understanding of the crystallisation processes occurring in the hafnium systems and so the need to study bulk powders to obtain this information. However, the results show that the system is quite complex and that more work needs to be carried out to fully understand the crystallisation mechanism. EELS is a good method for understanding the local chemistry, structure and bonding in both bulk powders and gate stacks but preliminary results show that much still needs to be understood about these systems and that combination with modelled EELS spectra is essential.

Acknowledgements

EPSRC for funding, Andrew Payzant at the CNMS and Richard Sweeney at Imperial College London.

References

[1] MacKenzie M, Craven A J, McComb D W and De Gendt S, J. Electrochem. Soc. 2006 153 F215
[2] McComb D W, Craven A J, Hamilton D A and MacKenzie M, APL 2004 84 4523
[3] Triyoso D H, Tobin P J, White B E, Gregory R and Wang X D, APL 2006 89 132903
[4] McGilvery C M, McFadzean S, MacKenzie M, Docherty F T, Craven A J, McComb D W and De Gendt S IoP Conference Series, MSMXV conference, April 2007, in press
[5] Garvie R C, J. Physi. Chem. 1965 69 1238
[6] Shukla S and Seal S, Int. Mater. Rev. 2005 50 45