Understanding and preventing beam damage effects in partially processed high-$k$ gate stacks

F T Docherty$^1$, M MacKenzie$^1$, D Pennicard$^1$, A J Craven$^1$ and D W McComb$^2$

$^1$Dept. of Physics and Astronomy, University of Glasgow, Glasgow G12 8QQ, UK.
$^2$Dept. of Materials, Imperial College London, London SW7 2AZ, UK.

E-mail: f.docherty@physics.gla.ac.uk

Abstract. Electron beam damage effects on a partially and a fully processed HfO$_2$ gate stack on silicon substrates are investigated, and their origins and prevention are discussed. Growth of silica between the silicon and hafnia layers is observed for the partially processed sample but is not seen for the fully processed wafer. Two sources of oxygen are found to react with the substrate to form silica. One is from the glue used in sample preparation. The oxygen from this source can be prevented from diffusing to the substrate by putting a gold barrier layer between the stack and the glue. The other source seems to come from the amorphous HfO$_2$ layer. Using a cooling rod sufficiently slows the diffusion rate so that growth is no longer observed.

1. Introduction

The International Technology Roadmap for Semiconductors [1] identifies the needs and challenges facing the semiconductor industry over the next fifteen years. It predicts that by this year, the SiO$_2$ gate oxide layer in CMOS devices will have decreased to the point where leakage current due to tunnelling through the oxide layer will become the limiting factor for devices used in portable applications. Consequently there is great urgency to find a suitable dielectric material with a higher permittivity, $k$, which will provide the same gate capacitance as a smaller thickness of SiO$_2$, but which will have a greater physical thickness and a resultant lower leakage current from tunnelling.

SiO$_2$ grows directly on Si but alternative high-$k$ materials must be deposited, e.g. by atomic layer deposition or chemical vapour deposition. The deposition and subsequent processing steps can affect the chemical and physical properties of the high-$k$ layer and determine the overall properties of the gate stack. Nanoanalytical electron microscopy, in particular the fine structure available in electron energy-loss spectroscopy, is a very useful technique to study wafers containing these materials. For example, it can be used to examine the local chemistry, structure and bonding, at the sub-nanometre scale, of the upper and lower interfaces of the high-$k$ layer, e.g. [2-5]. The samples can be studied at each step in the fabrication process and the effect of key processing stages can be determined.

Ideally, when a high-$k$ material is used, there should be no SiO$_2$ present since this adds to the equivalent oxide thickness. However, a small, controlled amount of SiO$_2$ has the potential benefit of maintaining high mobility in the channel by preventing the scattering that can result at the interface between the substrate and high-$k$. The actual amount of SiO$_2$ that forms between the substrate and high-$k$ layer is ideally controlled by the pre-treatment of the substrate, but subsequent processing steps include high temperature annealing in oxygen-rich atmospheres, can potentially induce further SiO$_2$ growth. Electron microscopy can be used to investigate the effect of processing steps on the width of
the SiO₂ layer at various stages of the process and this can be correlated to the electrical properties of the gate stack.

HfO₂ is one of the leading candidates to replace SiO₂. We have observed growth of the SiO₂ layer between the silicon substrate and HfO₂ layer when this region is irradiated by the electron beam in the electron microscope. Whilst it is possible to image using low doses that do not appear to induce SiO₂ growth during timescales required for imaging, it is not practical to use such low doses for nanoanalysis. Therefore it is crucial to eliminate beam damage effects so that we can be confident that any observation of increasing thickness of this layer is as a result of its formation during a processing step rather than in the microscope. Here we investigate the mechanism by which SiO₂ forms in the microscope and try to determine the source of oxygen. We investigate if a partially or fully processed wafer is more sensitive to in-situ growth and explore ways to inhibit electron-induced SiO₂ growth.

2. Materials and methods
The gate stack studied consisted of 4nm HfO₂ and 200 nm of poly-Si deposited on a Si substrate with a chemical oxide layer approximately 0.8 – 1.0 nm thick. The processing steps comprised of cleaning the wafer, atomic-layer deposition of the HfO₂ layer, a post-deposition anneal at 500°C in an oxygen atmosphere, deposition of a doped poly-Si layer, and a further anneal at 1000°C to activate the dopant.

Cross-sectional TEM specimens were prepared using grinding, polishing, dimpling and ion-milling. They were examined in a FEI Tecnai F20, operated at 200kV.

3. Results and discussion
Figures 1a and 1b show high-resolution images of an as-deposited HfO₂ sample taken as soon as the sample was first irradiated by the electron beam, and an image taken after the sample had been exposed to a dose of 9.1 x 10⁹ electrons / nm², respectively. In this case the HfO₂ has been deposited and no further processing steps have been taken. It can be seen that there is significant growth of the SiO₂ layer between collection of images, which is formed by consumption of the silicon substrate. Figures 1c and 1d show images taken from a fully processed stack at the beginning and end of exposure to a dose of 1.2 x 10⁹ electrons / nm². For the fully processed sample there appears to be no growth of the SiO₂ layer, whereas there was significant SiO₂ growth in the partially processed stack when it had received this lower dose. It is also interesting to note that the as-deposited HfO₂ is initially amorphous and crystallises in the electron beam. Crystallisation normally occurs in these samples during the next processing step, which is a post-deposition anneal.

![Figure 1. TEM images of an as-deposited HfO₂ sample (a) as soon as it is irradiated by the electron beam and (b) after exposure to a dose of 9.1 x 10⁹ electrons / nm², and a fully processed gate stack (c) immediately after it is first irradiated and (d) after exposure to a dose of 1.2 x 10⁹ electrons / nm².](image-url)
HfO$_2$ layer by the electron beam. The magnitude of the second, slower rate is around a fifth of that of the initial fast rate.

For the samples examined there was a large variation in the initial SiO$_2$ width, from 0.4 – 1.8 nm. The initial width was largest close to the hole in the specimen and this may be a sample preparation artifact. The initial SiO$_2$ width was found to be thinnest in the thickest parts of the sample. The interface is likely to be rougher in thick samples, so the initial width may be consequently underestimated. However, the trends observed for the growth of the SiO$_2$ layer were found to be independent of the initial SiO$_2$ width for all samples studied.

To determine the source of the oxygen reacting with the silicon substrate to form SiO$_2$ we attempted to investigate if the oxygen reached the substrate by a bulk or surface diffusion mechanism. To do this the data sets for the as-deposited HfO$_2$ sample, whose results are shown above, were collected firstly close to the hole in the sample and then moving away from the hole into progressively thicker regions of sample. If the oxygen migrates by a bulk diffusion mechanism the SiO$_2$ growth rate should be independent of sample thickness, whereas a sample thickness dependency indicates a surface diffusion mechanism. For the rates shown in Figure 2d for as-deposited HfO$_2$, the fastest initial rate is from the data collected at the thinnest part of the sample and the rates progressively decrease as the sample get thicker, indicating a surface diffusion mechanism. Similar behaviour is observed for the second, slower rates for the as-deposited HfO$_2$ sample. The second rate is always around a fifth of the initial fast rate no matter how thick the sample is.

One potential source of oxygen which could move by surface diffusion is from the glue used in sample preparation. Fig 1 shows that the glue is directly in contact with the HfO$_2$ layer in the partially processed wafer and is close to the silicon substrate. In the case of the fully processed wafer there is a large poly-silicon layer between the glue and the substrate. To determine if oxygen from the glue is used in the formation of SiO$_2$ in the as-deposited HfO$_2$ case, a sample was made with a 15nm gold barrier layer between the glue and wafer. Fig 1c shows that for this sample only one growth rate is observed. This growth period typically ends when the HfO$_2$ layer in the sample crystallises. After this point there is no further growth of the SiO$_2$ layer. Figure 1d shows that the growth rate is comparable.
to the slow growth rate observed for the partially processed sample with no gold barrier layer. However, there are also some data points for the fast growth rate for the sample with no gold barrier that fall into this range. It has already been mentioned that the rates are dependent on sample thickness. Therefore more work is required to determine how dominant the contribution of the oxygen from the glue is.

The source of oxygen giving rise to the other growth rate may come from trapped oxygen or water in the amorphous HfO$_2$ layer. It is known that amorphous HfO$_2$ is porous and hydrophilic. The annealing processing step would drive this water out and it would not be absorbed so easily after the HfO$_2$ crystallises. Therefore there would be no further growth after crystallisation, which agrees with experimental observations.

Any oxygen present in the sample in the early stages of the fabrication process is difficult to remove. The alternative way to prevent formation of SiO$_2$ in the electron microscope is to immobilise the oxygen source. An as-deposited sample with a gold barrier was placed in a liquid nitrogen cooled rod, the top of which was at a temperature of -73°C. No growth of the SiO$_2$ layer was observed after the sample had received a comparable electron dose to the earlier experiments. The HfO$_2$ layer crystallised in the beam at low temperature but no SiO$_2$ grow was observed prior to crystallization, in contrast to the growth previously observed for the as-deposited sample with and without the gold barrier. This shows that cooling the sample sufficiently slows down the oxygen diffusion rate to be able to analyse the sample without inducing SiO$_2$ growth.

4. Conclusion

This work has shown that there are two mechanisms responsible for the growth of SiO$_2$ in as-deposited HfO$_2$ samples, irradiated in the electron microscope. One source is the glue used in sample preparation. Oxygen from this source can be prevented from reaching the substrate by placing a physical barrier of gold between the glue and the stack. The second source may arise from oxygen in the amorphous HfO$_2$ layer. This can be immobilized by cooling the specimen to decrease the oxygen diffusion rate to the extent where diffusion is negligible over the typical timescales of interest. Electron-beam induced SiO$_2$ growth is not observed in a fully processed wafer. It is thought that this is because excess oxygen in the HfO$_2$ layer is driven out during the annealing step, which results in the crystallization, and also that the poly-Si layer presents a physical barrier to prevent oxygen from the glue diffusing to the substrate. Therefore it is critical that potential beam damage effects are considered when evaluating SiO$_2$ widths in partially processed gate stacks for accurate interpretation of the effects of processing steps for correlation with electrical characterization measurements.

Acknowledgements
Dr S de Gendt and his colleagues at IMEC for supplying the gate stack samples; Mr B Miller for preparing the TEM specimens.

References
[1] ITRS 2001 International Technology Roadmap for Semiconductors (San Jose, Semiconductor Research Association) http://www.itrs.net/Common/2004Update/2004Update.htm
[2] Craven A J, MacKenzie M, McComb D W and Hamilton D A 2003 *Inst. Phys. Conf. Ser.* 84 4523-25
[3] Lu J, Aarik J, Sundqvist J, Kukli K, Harsta A and Carlsson J-O 2005 *J. Cryst. Growth* 273 510-514
[4] Foran B, Barnett J, Lysaght P S, Agustin M P, and Stemmer S 2005 *J. Elec. Spec. and Related Phenomena* 143 149-158
[5] Craven A J, MacKenzie M, McComb D W and Docherty F T 2005 *Microelec. Eng.* 80 90-97