Analysing interface reactions using EELS

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Abstract. Using EELS spectrum imaging, an HfN or Hf(O,N) reaction layer has been identified at the TiN/HfO\textsubscript{2} interface in a metal inserted high-k gate stack. The reaction layer has a mean thickness of 0.45nm over an 18nm length of the interface. This reaction layer formed in the original HfO\textsubscript{2}. By binning the data $\times 4$ along the interface, a variation of the width from 0.35nm to 0.65nm along the interface can be seen. The 10%-90% widths of the elemental profiles can also be found but the binning required is greater ($\times 10$). The profile widths are approximately constant along the interface but the values differ from element to element. Thus the reaction has not formed a conformal layer of uniform thickness. An efficient way of processing the data at different levels of binning is described.

1. Introduction

As structures and devices become smaller, interfaces and surfaces play an increasingly important role in determining their properties. Since the layers are frequently polycrystalline, the interface may not be atomically flat. This is typical of many of the interfaces found in technologically important systems and so the ability to characterise such “rough” interfaces on the sub-nanometre scale is crucial.

Even if the average plane of such an interface can be made accurately parallel to the electron probe axis, which is often not the case, the electron probe will sample several layers as it traverses the interface region. This is the result of effects such as interface roughness and beam spreading. Thus interpretation of the image and spectroscopic data obtained is a major challenge. Here we discuss how the data from a standard EELS spectrum image, obtained using a NION UltraSTEM equipped with a Gatan ENFINA spectrometer, can be analysed to provide key information on a reaction at the HfO\textsubscript{2}/TiN interface in a TiN inserted HfO\textsubscript{2} high-k gate stack on Si. This reaction was first suspected and commented on in references [1,2].

A key problem is to ensure that the specimen is not modified by the electron fluence. This condition sets a limit to the spatial resolution that can be achieved. This limit depends on the signal-to-noise ratio required to extract the information and this, in turn, depends on the type of information sought. Once acquired, the signal-to-noise ratio can be improved by binning the data at the expense of spatial resolution. If the mean interface position can be aligned parallel to one edge of the data set, the data can be binned in the direction parallel to the interface. In this way, the spatial resolution is preserved across the interface and lost along it. What is required is an efficient method of processing the data with different levels of binning so that the optimum binning can be chosen for the extraction of a given type of information. An approach to this is discussed below.
2. Experimental details
The details of the deposition and processing of the high-k gate stack are given in references [1,2]. A sample for STEM was prepared using an FEI Nova 200 Dualbeam focused ion beam/SEM with a Sidewinder ion column and in-situ lift-out. The final thinning was carried out at 2kV, resulting in a lamella with \( t/\lambda \) in the range 0.3-0.4 at 100kV accelerating voltage. This lamella was examined in a Nion UltraSTEM at 100kV with a probe half-angle of 36mrad and an EELS collection half-angle of 36mrad. Figure 1 is a bright field image of the interface.

Figure 2a shows the survey image on which the regions used for a spectrum image and for drift correction are shown. The spectrum image had 36×188×1340 voxels with a pixel step of 0.1nm, an energy step of 0.3eV and a dwell time per step of 50msec. The voltage on the flight tube of the spectrometer was changed by a random amount after every spectrum so that the fixed pattern noise would be reduced when spectra were added together [3]. The spectra were corrected for the change in the flight tube voltage after acquisition, requiring the number of channels per spectrum to be reduced from 1340 to 1182 to remove end effects. During acquisition, spatial drift was corrected after every 10 lines. Figure 2b shows the HAADF image recorded as part of the dataset, showing the steps in position introduced by the drift correction. The dataset was aligned line by line using the contrast change at the interface. Figure 2c shows the resulting HAADF image. At this stage, the dataset has been reduced to 30×180×1182 voxels in size. The reduction to 30 in the horizontal direction was required to remove edge effects resulting from the alignment while the reduction to 180 in the vertical direction was chosen to give a value with a large number of factors so that the data could be binned by different amounts. Principal component analysis was applied to this dataset. The resulting components proved difficult to interpret physically. However, by reconstructing the data using only 10 components, the noise in the background was reduced significantly [4].

To avoid having to repeat the processing for each level of binning, extended datasets were constructed from the original data and the reconstructed data. These each contained the unbinned data and data binned by 2, 3, 4, 5, 6, 10, 15, 20, 30, 90 and 180. For the 20× binning, four starting positions (lines 0, 4, 9 and 14) were selected to allow the investigation of the positioning of the binning boundaries. A schematic of the resulting extended dataset, 30×513×1182 voxels in size, is shown schematically in Figure 2d.
The weak Hf N\textsubscript{2,3}-edge at 380eV lies just before the N K-edge (ca 400eV). A power law background model was fitted in a region prior to the Hf edge on the extended PCA reconstructed dataset. The backgrounds obtained were subtracted from the extended original dataset so that no information in the edges was lost due to the limited number of components in the reconstruction. The Hf signal was integrated up to the N edge onset. Using the same background subtraction, the N K-edge intensity was integrated over a 54 eV window from its onset. No correction was made for the small contribution from the Hf N\textsubscript{2,3}-edge. A check was made to confirm that correction was always small. This was done by subtracting a suitably scaled Hf N\textsubscript{2,3}-edge from a region of HfO\textsubscript{2}. A power law background was fitted before the Ti L\textsubscript{2,3}-edge and its intensity integrated over 70 eV window from its onset. The same procedure was used for the O K-edge but the integration window was over 22eV.

For the intensity and fit coefficient profiles, it is useful to define a mid-point (the 50\% height) and a profile width (the separation of the 10\% and 90\% heights). The 0\% and 100\% heights are defined as the value in the bulk material on either side of the interface. The experimental profiles have noise and so, to give a consistent measure of the heights, a function was fitted to each profile. The function chosen consisted of the sum of two sigmoids with independent mid-points and widths but constrained to change from 0 to 100\%.

3. Results and discussion

Figure 3 shows the elemental profiles across the interface for the fully binned data. Small errors in the background subtraction caused the Hf and O signals to go slightly negative in the bulk TiN on the right hand side. Offsets were added to bring them to zero. The profiles were then scaled to have the same value at the left (Hf and O) and right (Ti and N) sides. It is clear that the N profile is to the left of the Ti profile and the O profile is to the left of the Hf profile. The Hf and Ti profiles cross at around the 50\% level as do the O and N profiles. The relative shift of elemental profiles identifies the presence of a reaction layer \cite{1,2}. The separation of the profiles at the 50\% heights is \( \approx 0.45\) nm and so there is an HfN or possibly Hf (N,O) reaction layer of this width at the interface. Since the light element 50\% heights are to the left of the metal ones, the reaction has been a “nitridation” of the original HfO\textsubscript{2} rather than an “oxidation” of the subsequent TiN.

The separation of the 50\% heights is a measure of the average width of the reaction layer along the interface. Since double sigmoid fitting has been carried out on the extended dataset, the loci of the 50\% heights as a function of position along the interface can then be examined as a function of the degree of binning. Figure 4a shows the loci for \( \times 4 \) binning along the interface. Even with this modest level of binning, it can be seen clearly that the positions of the Ti and Hf profiles are always close together, as are those of the O and N profiles. It is also clear that the interface layer is wider in the top part of the interface (\( \approx 0.65\) nm) than it is in the bottom part (\( 0.35\) nm).

Figure 4b shows the separation of the 10\% and 90\% heights of each profile, which gives a measure of the profile width. The positions of these heights, and thus the profile widths, are much more susceptible to noise in the original data. Even with the dual sigmoid fits and \( \times 10 \) binning, there is still considerable scatter in the values of the separations. Nonetheless, it is clear that the widths of the profiles are relatively constant along the interface. The O profile (\( \approx 1.8\) nm) is wider than those of the Hf and Ti profiles (\( \approx 1.2\) nm) while that of the N profile is intermediate (\( \approx 1.4\) nm). These are all considerably wider than the width of the interface layer, showing clearly that such interface layers can be detected even if they are much narrower than the widths of the corresponding elemental profiles.
The width of the profiles is the result of a number of effects e.g. beam spreading and interface roughness. Since beam spreading would affect all the profiles in a similar way, the differing values of the profile widths is providing information on the nature of the HfO$_2$. “HfN” and the “HfN”-TiN interfaces. The fact that the widths of the O and N profiles differ is providing information on the nature of the reaction that has occurred.

4. Conclusions
Using EELS spectrum imaging, an HfN or Hf(O,N) reaction layer, has been identified at the TiN/HfO$_2$ interface in a metal inserted high-k gate stack. The layer has a mean thickness of 0.45nm over an 18nm length of the interface. This reaction layer has formed in the original HfO$_2$. By binning the data ×4 along the interface, a variation of the width from 0.35nm to 0.65nm along the interface can be seen. The 10%-90% widths of the elemental profile can also be found but the binning required to overcome noise is greater (×10). The profile widths are approximately constant along the interface but the values differ from element to element. Thus the reaction has not formed a conformal layer of uniform thickness. To allow binning along the interface, the interface was aligned parallel to one edge of the dataset. To provide an efficient way of processing the data with different degrees of binning, extended datasets containing the original data and data binned to the different levels were constructed. In this way, the processing can be carried on all levels of binning at the same time and the appropriate level of binning can be easily identified.

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