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Nanoanalysis of a sub-nanometre reaction layer in a metal inserted high-k gate stack

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Abstract

Reactions at the interfaces can occur in metal inserted high-k gate stacks and are likely to evolve during device processing. Such reactions may affect the electrical properties of the stack and hence these could change during processing. The key interfaces are often not atomically flat and characterising the reaction layers on the near atomic scale required is a challenge. Aberration corrected scanning transmission electron microscopy (STEM) and spectrum imaging (SI) using electron energy loss spectroscopy (EELS) is used to characterise an HfN or Hf(O,N) reaction layer, ~0.25nm wide, between HfO_2 and TiN. This demonstrates the very significant advances in high spatial resolution characterisation made in recent years.

1. Introduction

The continued decrease in the size of MOSFETs requires the replacement of the Si(O,N) gate dielectric by one with a higher dielectric constant, *k*. To take full advantage of the high-*k* dielectric, the poly-Si traditionally used for the gate electrode must be replaced by a metallic gate to remove the effect of the depletion capacitance. A key requirements is a stable effective work function of the correct magnitude appropriate to either *p*-type or *n*-type devices. However, the effective work function can change with device processing and typically moves towards the mid-gap [1]. Many mechanisms might be responsible for such a shift. One is trapping a small amount of charge at the interface. This is something on which electron beam techniques are unlikely to provide significant information. Another possibility is an interface reaction resulting in structural or compositional change. Such reaction layers would be likely to evolve during device processing and this could lead to changing electrical properties. This is an area where electron beam techniques can provide crucial information.

Unfortunately, identifying a thin reaction layer at a rough interface poses a challenging analytical problem. Aberration corrected scanning transmission electron microscopy (STEM) combined with electron energy loss spectroscopy (EELS) can now provide detailed information about such sub-nm layers. In this study, the reaction layer between TiN and HfO_2 in a metal inserted high-k poly-Si gate stack ($Si/SiO_2/HfO_2/TiN/poly\text{-}Si$) is investigated showing that the dielectric has been nitrided. In the original work investigating such reactions, a clear Si(O,N) reaction layer between the TiN and the poly-Si was identified but the reaction between the HfO_2 and the TiN could barely be detected [2, 3]. The present work elucidates the composition of this reaction layer, showcasing major advances in nanoanalysis.

2. Experimental Method

A Si(100) wafer was etched in HF/H_2O 1:100 solution to remove the native oxide and then cleaned in an O_3/deionized water sequence, resulting in the growth of 1.0nm chemical oxide. HfO_2 was deposited in an ALCVD ASM International, The Netherlands, Pulsar 2000 reactor using an $HfCl_4/H_2O$ process at 300°C. 80 deposition cycles were used to give a nominal 3.5–4.0nm. The deposited film was given an oxidizing post-deposition anneal at 500°C for 1 min, which resulted in polycrystalline monoclinic HfO_2 [4]. 10nm of TiN was deposited by PVD after a standard degas treatment at 330°C for 40s. The PVD TiN was deposited using a standard DC sputtering process. The deposition conditions were as follows: no substrate heating; process nitrogen flow of 75sccm; backside Ar flow of 25sccm; 5mTorr pressure; 8000W DC power. Finally 100nm amorphous Si was deposited and activated by annealing at 1000°C for 10s during which the amorphous silicon crystallized into activated poly-Si. In depositing the layers, the wafer surface was exposed to the atmosphere of the clean room as it was moved from process tool to process tool and, in particular, after the HfO_2 anneal and the TiN depositions.

A specimen for STEM was made using a standard cross-section method with the final ion milling step at 500eV ion energy. It was examined in an aberration corrected NION UltraSTEM equipped with a Gatan ENFINA electron spectrometer. This instrument has an image resolution of 0.1nm and allows atomic resolution

bright field (BF), high angle annular dark field (HAADF) and EELS spectrum imaging. A spectrum image (SI) is the dataset recorded when one or more spectra are recorded at each spatial pixel of a scan [5, 6].

The UltraSTEM was operated at 100kV with a probe half angle of 36mrad and an entrance half angle at the spectrometer of 35mrad. A line spectrum image was recorded across the HfO_2:TiN interface along a line shown schematically on Fig. 1. The step size was 0.049nm and the dwell time was 1.2sec. Power law backgrounds were fitted under the N K- and Ti $L_{2,3}$-edges and the edge intensities integrated. Internal standards for the HfO_2 and the TiN were obtained by summing the spectra from the first three and last three pixels of the SI respectively. These spectra are assumed to be from the "bulk" phases. The internal standards were used to do a multiple linear least squares (MLLS) fit to the data in the spectrum image.

3. Results

Figs. 1 and 2 are simultaneous BF and HAADF images of the gate stack. It is clear that interfaces are not atomically flat. Fig. 3 shows the intensity profiles of N K- and Ti $L_{2,3}$-edges after scaling so that the intensities in the "bulk" are the same for both elements. The width of the transition from maximum to minimum signal as the interface is crossed is ~1nm, i.e. far wider than the reaction layer of interest. The width of the transition is the result of both the rough interface and the lateral spreading of the probe within the specimen. However, both profiles are affected in the same way. Thus, if the two elements stop at a sharp interface, their profiles will overlie exactly. Any relative shift of the profiles is a strong indication of a reaction layer and also a measure of its width. This approach was used previously to highlight and characterise the Si(O,N) reaction layer between the TiN and the poly-Si [2,3].

In Fig. 3, the N profile is systematically to the left of the Ti profile by ~0.25nm although the noise on the profile might raise doubts in the mind of a sceptic. To demonstrate that this is not simply noise, MLLS fitting was used to model the spectra using the spectrum shapes from the internal "bulk" TiN and HfO_2 standards. The fit coefficients are plotted as a function of position in Fig. 4, after normalising to the same maximum values. The MLLS fitting process also gives the residual of the fit at each pixel i.e. the difference between the experimental spectrum and the fit. There is a significant residual at the N K-edge. The profile of the residual at the N K-edge is also shown on Fig.4, normalised to the same maximum value. This indicates the width of the region over which the interface-specific signal makes a significant contribution to the total. This is comparable to the widths of the transitions in Fig. 1.

To improve the signal-to-noise ratio, the SI can be divided into strips, corresponding to the width of the residual profile, and the spectra within a strip added together. Fig. 5 compares the spectrum from the strip centred on the interface with that from the adjacent strip in the TiN. The spectra have been normalised to the same N K-edge intensity. The Ti $L_{2,3}$ intensity from the strip at the interface is clearly lower than that in the adjacent strip so that the N:Ti ratio is indeed greater at the interface, as suggested by Fig. 3. The O K-edge can also be clearly seen in the spectrum from the strip at the interface and comes from the HfO_2 sampled by the electron probe with a possible contribution from the interface reaction itself.

Further insight can be gained by looking at the fine structure on the N K-edge, as was done in the earlier work [2,3]. This structure reflects the effect of the neighbouring atoms on the empty density of states around the excited N atom. Hence the shape reflects the local chemistry. Fig. 6 compares the N K-edge shape from the interface strip with that from the adjacent strip. The changes in shape are subtle but show clear differences in intensity in the regions 402-407 eV and 420-427eV.

Fig. 7 compares the N K-edge shape from the strip adjacent to the interface with that from actual bulk TiN [7], showing good agreement in shape. Above ~415eV the spectra diverge in intensity. This divergence occurs because the spectrum from the actual bulk TiN has been deconvoluted to remove the effect of multiple inelastic scattering, whereas the spectrum from the strip has not. Multiple inelastic scattering occurs when the electron traversing the specimen undergoes more than one inelastic scattering event. The most likely second event is excitation of a plasmon. This causes some of the edge intensity to be shifted to higher energy and results in the observed divergence of intensities. Deconvolution removes this shift to higher energies mathematically.

Fig. 8 compares the edge-shape from the interface strip with those from actual bulk TiN and HfN [7]. There is a similar divergence of intensities between the deconvoluted spectra from the bulk materials and the un-deconvoluted spectrum from the interface, as expected. The shape from the interface has characteristics of both

TiN and HfN. Thus, at the interface, the probe samples TiN, HfO_2 and a reaction layer of HfN or possibly Hf(O,N). The width of this reaction layer is the relative shift of the Ti and N profiles in Fig. 3 and is ~0.25nm.

4. Conclusions

The improved resolution, stability and probe current of an aberration corrected STEM allows the detection and characterization of sub-nanometre interaction layers. These capabilities have been used to demonstrate characterisation of an HfN or Hf(O,N) layer ~0.25nm wide at a rough interface. Such a reaction layer would be quite susceptible to change during device processing and might well contribute to the instability often observed in the value of the effective work function. The data processing techniques developed here can be taken further. The techniques and approach developed are applicable to a wide range of materials problems in the field of semiconductors and elsewhere.

Acknowledgements

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Figure Captions

Fig.1: BF image of the gate stack. The line shows a typical position for an SI across the interface.

Fig.2: Simultaneous HAADF image.

Fig.3: Elemental profiles across the interface normalized to the same intensities in the "bulk" and showing the ~0.25nm shift of the N relative to the Ti.

Fig.4: MLLS fit coefficients for "bulk" TiN and HfO_2 standards together with the profile of the residual at the N K-edge showing where the interface signal is significant

Fig.5: Comparison of the spectra from the interface and the adjacent "bulk" TiN normalized to the N K-edge intensity, confirming excess N at the interface. The O K-edge intensity at the interface is from the overlying HfO_2.

Fig.6: Comparison of the N K-edge shapes from the strip at the interface with that from the strip adjacent to the interface.

Fig.7: Comparison of the N K-edge shapes from the strip adjacent to the interface and from actual bulk TiN. The intensities diverge above 415eV because the TiN data has had multiple scattering removed while the SI data has not.

Fig.8: Comparison of the N K-edge shape from the strip at the interface with those from actual bulk TiN and HfN. The spectra from the bulk TiN and HfN have had the effects of multiple scattering removed while the SI data has not.

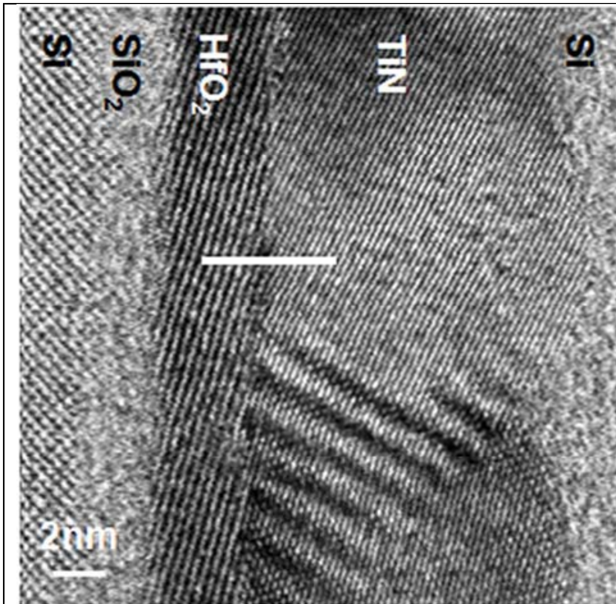

Fig 1

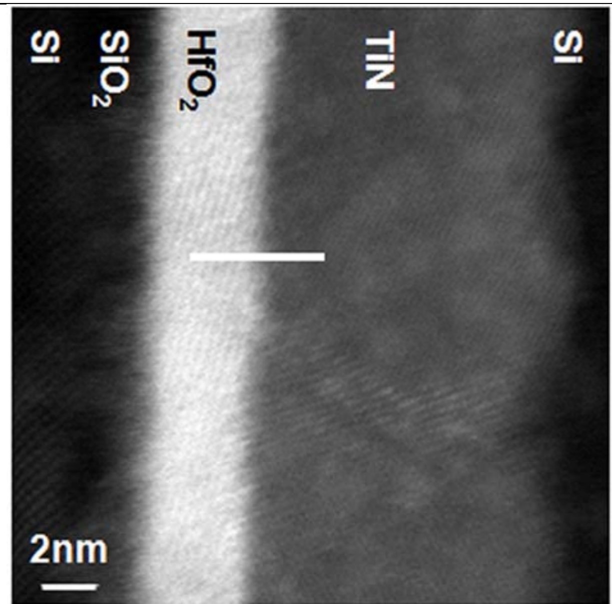

Fig 2

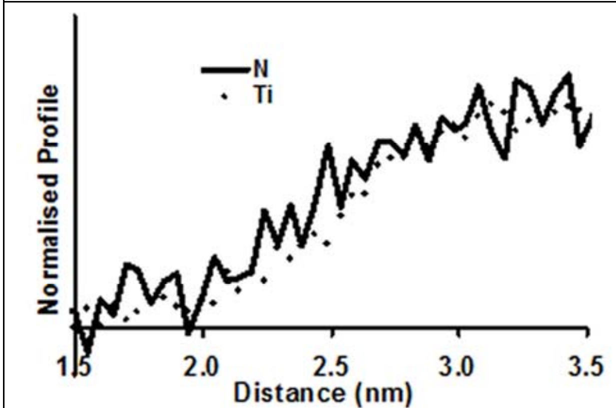

Fig 3

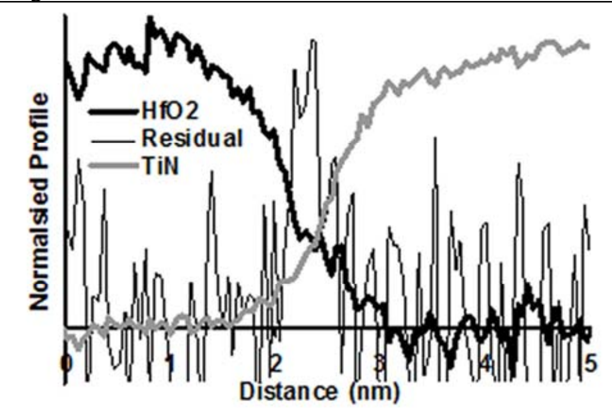

Fig 4

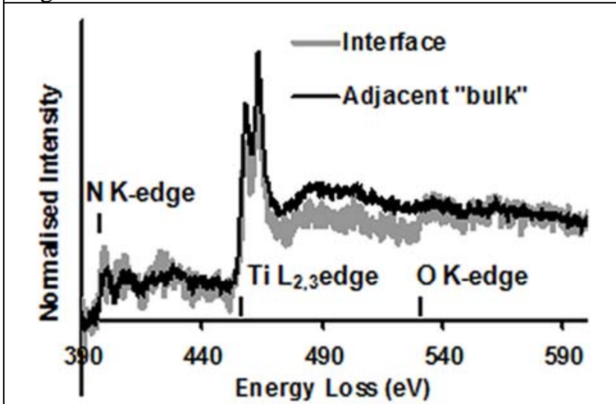

Fig 5

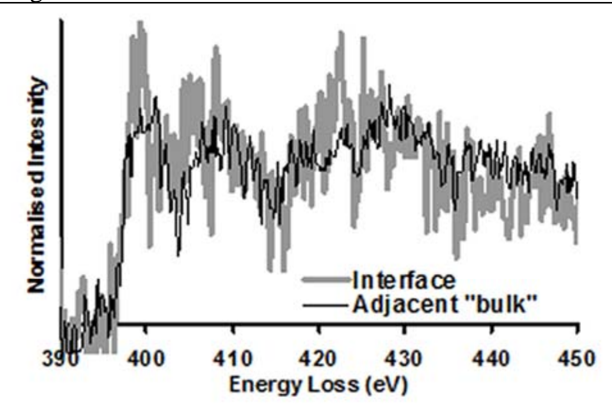

Fig 6

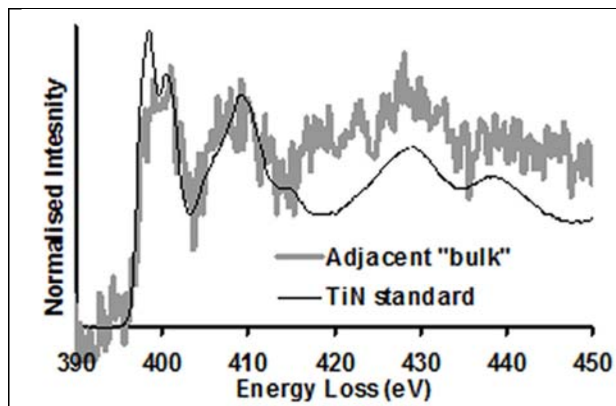

Fig 7

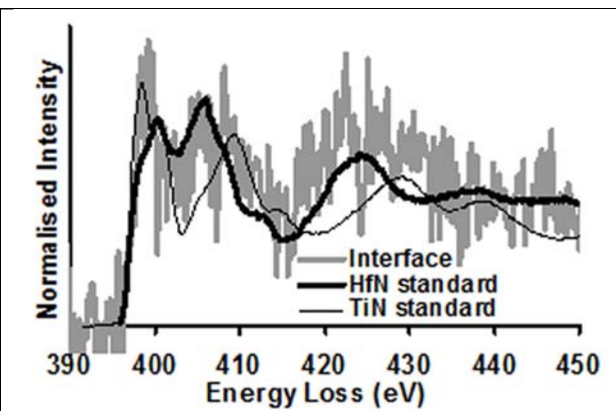

Fig 8