(S)TEM analysis of the interdiffusion and barrier layer formation in Mn/Cu heterostructures on SiO$_2$ for interconnect technologies

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Abstract. Mn/Cu heterostructures thermally evaporated onto SiO$_2$ and subsequently annealed were investigated by transmission electron microscopy (TEM) related techniques in order to study the diffusion interactions which lead to barrier layer formation. Electron energy loss spectroscopy provide evidence for the interdiffusion between the Mn and Cu layers following a 450 °C anneal, where the Mn diffuses towards the surface of the structure, while Cu diffuses towards the Mn/SiO$_2$, surrounding metallic Mn clusters but not propagating into the dielectric. The chemical composition of the 2-3 nm interfacial layer is primarily a mixture of +2 and +3 Mn valencies, in good agreement with previously reported results.

1. Introduction

Copper has progressively become the material of choice for transistor interconnects in the current processing technology for semiconductor devices; mainly due to its lower resistivity and improved electromigration damage compared with aluminium. However, the high diffusion rates between Cu and the silicon oxides or polymers used as insulating layers requires the introduction of physical barriers to prevent interdiffusion across the interface. These barriers are commonly made of a stack of Ta/TaN layers, but they present a poor electrical conductivity and increase the total resistance of the interconnect. Therefore, there is a need to reduce the thickness of the barriers while still preserving their efficiency, high quality interfaces and adhesion to the adjacent layers. Moreover, as the semiconductor industry moves towards the 32 nm technological node, these barriers are no longer a viable option and other approaches have to be developed.

Cu(Mn) self-forming diffusion barriers have become a promising option to overcome these problems. Their formation process involves the deposition of a Cu(Mn) alloy directly onto the SiO$_2$ layer and after annealing, the alloying element segregates towards the interface chemically reacting with the insulator. The result is the formation of a Mn$_x$(Si)O$_y$ thin barrier layer (2-3 nm[1]) that can avoid the diffusion of Cu into the SiO$_2$. These layers have already been proven to be effective, but unfortunately the information about their exact nature and composition still remains limited and in some cases contradictory [2-4]. All this discrepancy may arise from the fact that all these studies have been performed so far on Cu(Mn) alloys, but the basic elemental interactions, rather than the alloy interactions, between pure Mn and the substrate layer have not been considered yet. Therefore, the
chemical interaction between pure metallic Mn and SiO$_2$, and the basic interaction between metallic Cu and Mn as a function of annealing could reveal important information.

2. Experimental
A series of samples consisting of 30 nm of metallic Mn capped with 20 nm of metallic Cu were grown by thermal evaporation in a Leybold Univex Chamber at a vacuum pressure of $2 \times 10^{-6}$ mbar. The substrates employed were 600 nm of amorphous SiO$_2$ on Si(001) and the samples were studied after annealing at 450 °C for 2 hours at a pressure of $10^{-8}$ mbar. Conventional transmission electron microscopy (TEM), high resolution TEM (HRTEM), high angle annular dark field (HAADF) and EELS were carried out in a JEOL 3000 and a Tecnai Osiris electron microscopes operating at 300 kV and 200 kV respectively. Samples in cross section geometry were prepared by the conventional method of grinding and polishing followed by Ar$^+$ ion milling in a Gatan PIPS until electron transparent.

3. Results
In Figure 1, a low magnification conventional TEM micrograph of the heterostructure is displayed. In all the areas of the sample, continuous layers with smooth interfaces and good adhesion to the substrate are observed. The Mn layers have a more uniform thickness while the Cu layer displays a higher degree of roughness which is attributed to its bigger average grain size. HAADF micrographs of this sample show an unexpected bright contrast in a region approximately 10 nm thick above the interface between the Mn layer and the SiO$_2$. Since the difference in contrast in the images obtained with this technique is directly related to the difference in Z number of the elements that are present, these brighter regions must contain an element or compound with an average Z number higher than Mn.

To confirm this, EELS elemental maps were recorded in STEM mode of the different layers. The nominal size of the probe used is 1 nm and the maps contain 100x100 pixels. The extracted signal of the different elements is obtained after background subtraction and noise reduction by a multivariate statistical analysis [5]. A Hartree-Slater step function was considered to take into account the effects of sample thickness and the remaining signal under the peaks was integrated. The results of the application of this procedure for Cu $L$, Mn $L$ and O $K$ peaks are shown in Figure 2 a)-c). A relatively large amount of Mn can be found in the Cu layer as expected; but also segregation of Cu into the Mn layer has occurred. This segregated Cu tends to encapsulate areas of the Mn layer close to the interface, where a higher Mn signal and lower O is found. Since the oxygen arises from the exposure of the TEM sample to environmental conditions, and is more accentuated in the Mn layer with the exception of these regions, this means that the segregated Cu is preventing these encapsulated areas from being as heavily oxidized as the rest, and as a consequence the metallic Mn signal is stronger.
An important fact to highlight is that no trace of Cu is found in the SiO$_2$ layer, which can be attributed to the formation of an effective diffusion barrier layer.

![Figure 2: EELS extracted signal elemental maps for a) Cu L b) Mn L and c) O K edges. Squares in b) indicate the position where the spectra shown in Figure 3 were taken.](image)

Finally, the nature of the chemical reactions at the Mn/SiO$_2$ interface to form a diffusion barrier are now explored by EELS. Here we have estimated the Mn peaks I($L_3$)/I($L_2$) intensity ratio after background subtraction to investigate possible variations of the Mn valence state along the layer. Firstly, due to the lack of available data in the literature for typical EELS spectra of metallic manganese, reference spectra were taken from a sample consisting of deposited Mn kept under vacuum conditions during the whole process to avoid oxidation. An example is displayed in Figure 4, where an average intensity ratio of 1.23±0.2 was calculated. For the valence state of Mn in different oxides, we rely on the data from Schmidt et al. [6].

![Figure 3: EEL spectra recorded in the Mn layer at different positions from the interface, and metallic Mn taken as reference. In the inset, variation of the intensity ratio I$_2$/I$_3$ in the interfacial region indicating different valence states for Mn.](image)

Figure 3 displays several point spectra which were recorded at different positions through the lower half of the Mn layer in the sample starting from the Mn/SiO$_2$ interface. From the calculated intensity ratios displayed in the inset in Figure 3, clear variations in the Mn oxidation state can be deduced. We can distinguish three different regions in the layer: the first one, with a thickness of 2-3 nm situated just above the interface, where the intensity ratio suggests a mixture of Mn valence of +2 and +3, consistent with the results reported by Otsuka et al. [4]. A second region (I$_3$/I$_2$~2.9) corresponds to the bulk Mn layer. Taking into account the results from Schmidt et al. [6], the relative intensities of the two peaks in this area should contain Mn$_3$O$_4$ (I$_2$/I$_3$=2.8) as the main constituent. However, as the surface of the original metallic Mn layer was oxidized due to the exposure of the sample to...
environmental conditions, we believe that the EEL spectra in that region do not correspond to those of a layer of Mn₂O₃ but to the overlapping of the spectra corresponding to metallic Mn (I₁/I₂=1.2) sandwiched between the layers of Mn oxides (I₃/I₂=3.9) along the beam path in XTEM. Finally, the third region is located in the encapsulated Mn area, where the measured intensity ratio (I₃/I₂≈1.7) suggests a higher content of metallic manganese in agreement with the EELS results.

4. Discussion
The diffusion of Mn in Cu in Cu(Mn) alloys have been widely reported in the literature, but to the best of our knowledge, no published data exists about diffusion of Cu in Mn in thick layered structures. We therefore propose that similar to copper diffusion in other metals, the polycrystalline nature of the Mn layer is the reason for the presence of Cu in this layer. The small average Mn grain size creates numerous paths for the migration of Cu atoms into the layer. Similarly, Mn would migrate to the Cu layer following the same mechanism. The 450°C anneal of the Cu/Mn layered structure results in the formation of metallic Mn clusters surrounded by a thin layer of Cu. For the upper layer, the migration of Mn atoms towards the surface of a Cu matrix is mainly enhanced by the presence of residual oxygen contamination [7] introduced in the deposition process and subsequent handling, to form MnO via the displacement reaction Cu₂O+Mn→2MnO during the vacuum annealing. Equivalently, for the solute Cu in the Mn matrix (lower layer), it is expected that Cu atoms will migrate to the interface Mn/SiO₂ to form a more stable oxide. However, these Cu atoms do not reach the dielectric, since the reaction between the Mn atoms and the SiO₂ at the interface leads to the formation of a MnSiO₃ self-formed barrier layer that prevents interdiffusion.

Acknowledgements
J. G. Lozano would like to acknowledge the support of the European Commission under the Marie Curie Programme 2009. Financial support from the SFI PI Program Science under the Grant No. 08/IN.1/I2052 is also acknowledged.

5. Conclusions
In summary, Mn/Cu heterostructures thermally evaporated onto SiO₂ and subsequently annealing were investigated by TEM related techniques. EELS results indicate the occurrence of interdiffusion between the Mn and Cu layers, where the Mn tends to diffuse towards the surface of the structure, and the Cu atoms diffuse towards the Mn/SiO₂ interface. EELS analysis would also indicate that the chemical composition of the 2-3nm interfacial layer is primarily Mn in +2 and +3 oxidation states, which is effective at preventing Cu diffusion into the dielectric layer.

References
[1] Koike J and Wada M 2005 Appl. Phys. Lett. 87, 041911
[2] Koike J, Haneda M, Iijima J, Otsuka Y, Sako H, Neishi K 2007 J. Appl. Phys. 102, 043527
[3] Ablett J M, Woicik J C, Tokei Zs, List S, Dimasi E 2009 Appl. Phys. Lett. 94, 042112
[4] Otsuka Y, Koike J, Sako H., Ishibashi K, Kawasaki N, Chung S M, Tinaka I 2010 Appl. Phys. Lett. 96, 012101
[5] Lozano-Perez S, de Castro V, Nichols R J 2009 Ultramicroscopy 109, 1217
[6] Schmid H K and Mader W 2006 Micron 37, 426
[7] Katayama I, Oura K, Shoji F and Hanawa T 1998 Jap. J. Appl. Phys. 27, L1822