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Chemical and structural investigations of the interactions of Cu with MnSiO₃ diffusion barrier layers

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X-ray photoelectron spectroscopy (XPS) has been used to investigate the thermodynamic stability of Cu layers deposited onto Mn silicate (MnSiO₃) barrier layers formed on SiO₂ surfaces. Using a fully *in situ* growth and analysis experimental procedure, it has been shown that ~1 nm Cu layers do not chemically react with ultra thin (~2.6 nm) MnSiO₃ surfaces following 400 °C annealing, with no evidence for the growth of Cu oxide species, which are known to act as an intermediate step in the Cu diffusion process into silica based dielectrics. The effectiveness of MnSiO₃ as a barrier to Cu diffusion following high temperature annealing was also investigated, with electron energy loss spectroscopy suggesting that a ~2.6 nm MnSiO₃ layer prevents Cu diffusion at 400 °C. The chemical composition of a barrier layer formed following the deposition of a partially oxidised Mn (MnO_x)/Cu alloy was also investigated using XPS in order to determine if the presence of Cu at the Mn/SiO₂ interface during MnSiO₃ growth inherently changes the chemical composition of the barrier layer. In contrast to previous publications, it has been shown that Mn oxide species do not form in the barrier region during thermal annealing, with Cu appearing to be chemically inert in the presence of Mn and SiO₂. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4752874>]

I. INTRODUCTION

Within the past ten years, copper has replaced aluminium as the metal of choice for interconnects in microelectronic devices, due to its lower resistivity and increased resistance to electromigration.^{1,2} However, in order to prevent interdiffusion between the Cu interconnect and the surrounding dielectric material, barrier layers are required.³ As device geometry continues to decrease, there is a need to develop a scaleable barrier layer technology alternative to the current industry standard of Ta/TaN. Self forming diffusion barrier (SFB) layers resulting from a chemical interaction between a deposited metal and the underlying dielectric material have been proposed as a possible method of barrier layer formation for future interconnect generations.²⁻⁴ Manganese silicate (MnSiO₃) SFB layers are viewed as a potential alternative to Ta/TaN barriers.^{5,6} Casey *et al.*^{7,8} have recently investigated the chemical composition of Mn silicate layers on SiO₂ surfaces and have shown that MnSiO₃ is the most thermodynamically stable product formed through the interaction of partially oxidised manganese (MnO_x, where $x < 1$) and SiO₂. While these studies by Casey *et al.*^{7,8} have focused on the growth of MnSiO₃ barriers in the absence of Cu, other studies^{9,10} have recently shown that the thermodynamic stability of Cu thin films on barrier layer surfaces is also of crucial importance to device performance. It is suggested by Rodriguez *et al.*⁹ and Willis *et al.*¹⁰ that oxidation of Cu interconnects acts as

an intermediate step in the Cu diffusion process into silica based dielectrics, given that the presence of copper oxide acts as a source of Cu ions available for diffusion. Therefore, it is essential that potential barrier layer candidate materials are chemically inert in the presence of Cu, particularly during thermal processing, in order to prevent the formation of Cu oxide.

In this study, x-ray photoelectron spectroscopy (XPS) is used to investigate the thermodynamic stability at high temperature of thin (~1 nm) Cu layers deposited onto ultra thin Mn silicate (MnSiO₃) barrier layer surfaces. Using a fully *in situ* ultra high vacuum (UHV) growth and analysis procedure, a ~2.6 nm thick MnSiO₃ barrier layer was formed in the absence of Cu. Following MnSiO₃ growth, a ~1 nm Cu layer was deposited on the surface and subsequently annealed to high temperature. *In situ* XPS was used to monitor the chemical composition of the deposited Cu layer following the thermal annealing cycles, in order to investigate the chemical interactions which occur between copper and Mn silicate at high temperature.

In addition to determining the thermodynamic stability of MnSiO₃ surfaces, the barrier layer properties of Mn silicate was also investigated. Following the completion of XPS analysis, a protective Cu capping layer (~10 nm) was deposited onto the surface, with the sample being removed from UHV and subsequently analysed using electron energy loss spectroscopy (EELS). While previous studies^{11,12} have used EELS analysis to determine if Mn based layers are an effective barrier to Cu diffusion as a function of thermal annealing, the experimental approach adopted in this study allows the same sample to be investigated using both *in situ* XPS

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and EELS in order to fully understand all aspects of sample growth and analysis.

While Sec. I of this paper focuses on MnSiO₃ layers formed using the traditional sequential barrier deposition process, it has been proposed^{11–13} that the deposition of Mn/Cu alloys may be more suitable for the growth of SFB layers in future micro-electronic devices. In this process, thermal annealing is used to cause Mn diffusion from the Cu solid solution towards the SiO₂ interface, which results in the formation of the barrier layer. In Sec. II of this paper, a separate study was performed in order to investigate the growth of Mn based barrier layers following the deposition of MnO_x/Cu alloys, in order to determine if the inherent interactions which occur due to the presence of Cu at the Mn/SiO₂ interface impact on the chemical composition of the barrier layer. The importance of this study lies in the discrepancies which currently exist within the published literature relating to the chemical composition of Mn barrier layers formed through the sequential deposition of Mn layers compared to results found following the deposition of Mn/Cu alloys. For example, previous studies^{3,7,8} have shown that the sequential deposition of Mn layers on SiO₂ results in the growth of MnSiO₃ layers free from both metallic Mn and Mn oxide species, while further publications^{6,11} have reported that the deposition of Mn/Cu alloys results in the growth of both Mn silicate and Mn oxide species within the barrier layer region. The work of Frederick *et al.*¹⁴ has suggested that the growth of metal oxide species due to the reduction of SiO₂ during barrier layer growth may result in the diffusion of un-bonded Si atoms into the Cu interlayer, causing an increase in interlayer resistance and an associated degradation in device performance. Furthermore, Gordon *et al.*¹ have suggested that adhesion properties of Cu layers on Mn silicate surfaces are superior to those of Cu on Mn oxide surfaces. Therefore, it may be preferential to limit the formation of Mn oxide species during the growth Mn silicate barrier layers on SiO₂ surfaces. As such, the focus of this study is to determine if the growth of Mn oxide species is due to inherent chemical reactions which occur following the deposition of Mn/Cu alloys, or alternatively, if this Mn oxide formation can be attributed to different methods of sample preparation and sample analysis.

II. EXPERIMENTAL DETAILS

High quality thermally grown SiO₂ layers on silicon, with a thickness of 5.4 nm, were grown using the Semitool dry oxidation process in a Thermoco 9002 series furnace at 850 °C. The SiO₂ surfaces were prepared using a standard degreasing procedure of successive dips in acetone, methanol, and isopropyl alcohol (IPA) before being loaded into a UHV deposition and analysis system. Samples were then degassed at ~200 °C for 2 h, with the UHV chamber reaching a maximum pressure of 5×10^{-9} mbar during degassing. The XPS analysis was carried out using a VG Microtech electron spectrometer at a base pressure of 1×10^{-9} mbar. The photoelectrons were excited with a conventional Mg K α ($h\nu = 1253.6$ eV) x-ray source and an electron energy analyser operating at a 20 eV pass energy, yielding an overall

resolution of 1.2 eV. High temperature annealing studies were carried out in vacuum at a pressure of 5×10^{-9} mbar, with samples kept at the target temperature for 60 min. As no further changes were observed in XPS spectra taken following high temperature annealing for an additional 60 min, it was assumed that chemical reactions reached thermodynamic equilibrium following these annealing cycles. However, it should be noted that the kinetics of these reactions were not investigated as part of this study.

Partially oxidised manganese thin film deposition was performed by evaporating metallic Mn at room temperature using an Oxford Applied Research EGC04 mini electron-beam evaporator, in an O₂ partial pressure of 5×10^{-8} mbar.⁷ Room temperature e-beam evaporation of copper thin films was performed using a Cu source material of 99.9% purity, at a deposition pressure of 5×10^{-9} mbar. MnO_x/Cu alloys were deposited onto SiO₂ surfaces through the simultaneous deposition of Mn and Cu from the mini e-beam source, in an O₂ partial pressure of 5×10^{-8} mbar. It should be noted that Cu 2p spectra taken from the MnO_x/Cu alloy are identical to that taken from a metallic Cu reference material and as such it is stated that the O₂ partial pressure used during alloy deposition did not result in oxidation of the Cu layer.

The XPS core level spectra were curve fitted using Voigt profiles composed of Gaussian and Lorentzian line shapes in a 3:1 ratio and using a Shirley-type background. The full width at half maximum (FWHM) of the Si 2p bulk peak was 0.9 eV, with SiO₂ and Mn silicate component peaks in the range 1.1 eV to 1.2 eV. The FWHM of the O 1s SiO₂ component was 1.2 eV with Mn silicate and Mn oxide peaks in the range of 1.2 eV to 1.1 eV.

It should be noted that curve fitting of the Mn 2p spectrum could not be performed given that XPS ghost peaks¹⁵ emanating from the Mn 2p^{1/2} are present within the peak profile of the Mn 2p^{3/2} component. As such, only non-curve fitted Mn 2p spectra are included in this study. In agreement with previous works,^{7,8} the Mn 2p spectra are primarily used to identify the presence of metallic Mn and oxidised Mn species on the sample surface, with O 1s and Si 2p spectra used to conclusively identify the presence of differing oxidised Mn species such as Mn silicate and Mn oxide. Furthermore, it should be noted that the behaviour of Mn atoms in a Cu alloy matrix has been reported to change the peak profile of the Mn 2p spectrum.¹⁶ Given that the spectral component resulting from the interaction of metallic Mn and Cu has a similar binding energy position to that of oxidised Mn, Mn 2p spectra are not used for interfacial chemical analysis in situations where both metallic Mn and Cu are present on the surface.

EELS in scanning-transmission electron microscopy (STEM) mode measurements were carried out on a JEOL3000 FEG microscope operating at 300 kV, with a nominal probe size of 1 nm. Samples in cross section geometry were prepared by the conventional method of grinding and polishing followed by Ar⁺ milling in a Gatan PIPS until electron transparent. The thickness of the MnSiO₃ barrier layer (2.6 nm) was measured using high resolution transmission electron microscopy (HRTEM) images, which are shown in a previous study.⁷

III. RESULTS AND DISCUSSIONS

A. Thermodynamic stability of Cu on MnSiO₃

Curve fitted O 1s and Si 2p core level spectra taken from the 5.4 nm thermal SiO₂ surface are shown in Figure 1, displaying Si 2p component peaks originating from both the SiO₂ layer (~104 eV) and the underlying silicon substrate (~99 eV). The corresponding spectra taken following the deposition of a ~1 nm partially oxidised Mn (MnO_x, where $x < 1$) thin film onto the SiO₂ surface at room temperature are also shown. Curve fitting analysis shows small changes to the core level profiles suggesting that Mn deposition resulted in the growth of additional component peaks in both the O 1s and Si 2p spectra separated from the SiO₂ components by 1.4 eV and 1.3 eV, respectively. These peaks are attributed to the presence of the Mn silicate species MnSiO₃, in agreement with previous photoemission results.^{7,8} In addition to this, the O 1s spectrum also shows evidence for a third component peak at a binding energy position of 530.0 eV, which is attributed to the presence of Mn oxide.^{7,17} The corresponding Mn 2p spectrum in Figure 2 clearly shows the presence of both metallic Mn and oxidised Mn spectral components, with curve fitting analysis suggesting a metallic Mn:oxidised Mn ratio of 5:1. Angular resolved Mn 2p spectra (not shown) show no evidence for spatial segregation between the oxidised and metallic species, indicating that the oxygen content is homogeneously distributed throughout the deposited film. Following deposition, the sample was annealed to 400 °C in UHV, resulting in the growth of Mn silicate as evidenced by the growth of MnSiO₃ component peaks in both the Si 2p and O 1s spectra. It should be noted that the O 1s spectrum taken following annealing suggests the full conversion of Mn oxide to Mn silicate, as previously reported.⁷ The corresponding Mn 2p spectrum in Figure 2 also shows the full conversion of metallic Mn to MnSiO₃, suggesting the formation of a MnSiO₃

FIG. 1. Curve fitted O 1s and Si 2p spectra taken following the formation of a 2.6 nm MnSiO₃ layer on SiO₂ and subsequent deposition of a ~1 nm Cu layer onto the MnSiO₃ surface.

FIG. 2. Mn 2p spectra, corresponding to Figure 1, show no evidence of chemical interaction between the Cu and MnSiO₃ layers following 400 °C.

barrier layer free from both metallic Mn and Mn oxide. As stated previously, the full conversion of metallic Mn to Mn silicate prior to Cu deposition is of significant importance as the interaction of metallic Mn and Cu¹⁶ is known to alter the profile of the Mn 2p photoemission peak, complicating chemical analysis. Therefore, in the absence of metallic Mn, the Mn 2p core level profile could be used to investigate any chemical interaction of MnSiO₃ with a deposited Cu layer.

A ~1 nm Cu thin film was deposited on the MnSiO₃ surface at room temperature using electron beam evaporation, with the Cu 2p spectrum taken from the surface shown in Figure 3. Comparison with a reference spectrum taken from a pure metallic Cu sample suggests that the deposited layer was in a fully metallic Cu state. The sample was subsequently annealed to 400 °C in order to determine the thermodynamic stability at elevated temperature of the Cu layer on MnSiO₃. Crucially, the profile of Cu 2p spectrum taken from the annealed surface following 400 °C annealing is identical to that of the Cu reference material, and as such there is no

FIG. 3. Cu 2p spectra, corresponding to Figure 1, show no evidence for chemical interaction between the Cu and MnSiO₃ layers.

evidence for the formation of Cu oxide species due to the high temperature annealing of Cu on MnSiO₃ surfaces. Si 2p and O 1s spectra taken from the surface following annealing, in Figure 1, show no changes in peak profile consistent with no chemical interaction occurred between the MnSiO₃ barrier layer and the annealed Cu film. Furthermore, the Mn 2p spectra in Figure 2 also show no changes in peak profile following 400 °C annealing supporting this conclusion.

The work of Rodriguez *et al.*⁹ has suggested that the formation of Cu oxide species on silica based dielectric surfaces acts as an intermediate step in the diffusion mechanism of Cu ions. As such, it is suggested that MnSiO₃ barrier layers may act to prevent the formation of Cu oxide species as a function of high temperature thermal annealing and therefore inhibit the diffusion of Cu into the underlying SiO₂ layer. However, it should be noted that the XPS technique has limited capability to investigate the effectiveness of MnSiO₃ as a barrier layer to the diffusion of Cu. Therefore, following the completion of XPS analysis a protective Cu capping (~10 nm) layer was deposited onto the surface, with the sample being removed from UHV and subsequently analysed using EELS.

Figure 4 shows EELS composition line profiles taken from this sample. The O K, Mn L, and Cu L signals were extracted after background subtraction and multivariate statistical analysis noise reduction, with the remaining signal under the corresponding peaks being integrated. The presence of three distinct regions is clearly revealed, namely the Cu capping layer, the MnSiO₃ barrier layer, and the underlying 5.4 nm thermal SiO₂ film. It can be seen that the line profiles show that the Cu L signal falls to zero within the silicate barrier region, to within the detection limit of the technique. Therefore, based on the combined XPS and EELS, it can be concluded that a MnSiO₃ layer with a thickness of ~2.6 nm is chemically stable in the presence of Cu and also acts as an effective barrier to Cu diffusion following 400 °C annealing. It should be noted that there is evidence for an overlap between the Mn L and Cu L line profiles at the interface between the Cu and the MnSiO₃ regions. However, it is suggested that this may be due to the nominal probe size of 1 nm

FIG. 4. Chemical composition profile taken across the Cu/MnSiO₃/SiO₂ interfacial region using EELS line scans.

used in this experiment, rather than evidence of Cu penetration into the MnSiO₃ layer.

B. Effect of Cu on the chemical composition of barrier layer growth

In order to investigate how the presence of Cu at the MnO_x/SiO₂ interface during MnSiO₃ barrier formation affects the chemical composition of the barrier layer, a ~2 nm alloy containing approximately 60% partially oxidised Mn and 40% Cu was deposited onto the 5.4 nm SiO₂ surface. Angular resolved XPS measurements showed no evidence of spatial segregation between the Mn and Cu, which suggests that the alloy was homogenous. It should be noted that the Mn:Cu ratio used in this experiment was considerably more Mn rich than that used in previous studies.^{11,12,18} However, in order to form a MnSiO₃ layer of sufficient thickness to be easily investigated using conventional XPS, the thickness of deposited Mn could not be reduced considerably below ~1 nm. Furthermore, the high surface sensitivity of XPS places an upper limit on the total alloy thickness which could be deposited without significantly attenuating the underlying Si 2p and O 1s core level spectra. Therefore, while the Mn:Cu ratio used in this experiment is different to that used in previous works, the study still serves to highlight the inherent chemical interactions which occur between Mn/Cu alloys and SiO₂ surfaces.

Figure 5 shows O 1s and Si 2p spectra taken from the SiO₂ surface before and after MnO_x/Cu alloy deposition. The spectra show evidence for the growth of Mn silicate (MnSiO₃) upon alloy deposition, in agreement with the results in Figure 1, while the O 1s spectrum again shows evidence for the presence of Mn oxide within the partially oxidised Mn film. In agreement with this, the Mn 2p in Figure 6 taken following alloy deposition clearly shows evidence for the presence of both metallic Mn and Mn oxide component peaks within the peak profile. As stated previously, changes

FIG. 5. Curve fitted O 1s and Si 2p spectra taken following the deposition of a ~2 nm alloy layer containing partially oxidised Mn (~50%) and metallic Cu onto SiO₂ surface and subsequent high temperature annealing.

FIG. 6. Mn 2p spectra, corresponding to Figure 5, could not be used to investigate the chemical composition of the barrier layer region due to the interaction between metallic Mn and Cu.

in the Mn 2p peak profile due to the interaction of metallic Mn and Cu complicate the analysis of the chemical state of Mn within the alloy. Therefore, it is difficult to accurately quantify the ratio of metallic Mn and Mn oxide species within the deposited film. However, given that this interaction does not affect the peak profile of the Cu 2p core level,¹⁶ it can be stated based on the Cu 2p spectrum in Figure 7 that the Cu present within the alloy is in the form of un-oxidised metallic Cu.

A series of high temperature vacuum anneals between 200 °C and 400 °C were performed on the sample and the O 1s and Si 2p spectra taken from these anneals are shown in Figure 5. These spectra show evidence for the growth of MnSiO₃ following thermal annealing to 200 °C and 400 °C, as evidenced by the growth of the component peaks at 531.3 eV (O 1s) and 102.6 eV (Si 2p), respectively. In addition to this, it can be clearly stated that the O 1s spectra in

FIG. 7. Cu 2p spectra, corresponding to Figure 5, taken following the deposition of a MnO_x/Cu alloy and subsequent high temperature annealing.

Figure 5 show no evidence for the growth of Mn oxide species within the barrier layer region. Furthermore, the spectra show the complete removal of the Mn oxide component peak following 400 °C annealing, due to the conversion of Mn oxide to MnSiO₃ in agreement with previous studies.⁷ The corresponding Cu 2p spectra shown in Figure 7 show no changes in peak profile following thermal annealing which again suggests that Cu does not chemically react at the Mn/SiO₂ interface. It should be noted that the Mn 2p spectra, shown in Figure 6, show evidence for the presence of residual metallic Mn species on the surface following thermal annealing to 400 °C. Angular resolved Mn 2p spectra (not shown) taken from the surface suggest that the residual metallic Mn species is surface localised with respect to both the deposited Cu and the Mn silicate barrier layer. This result is in agreement with previous studies⁵ which have shown that thermal annealing of Mn/Cu alloys results in Mn diffusion from the Mn/Cu solid solution and migrating towards both the underlying dielectric interface and also towards the surface of the alloy film. As such, it is suggested that the residual metallic Mn seen in Figure 6 is indicative of the presence of Mn which segregated to the alloy surface following thermal annealing.

Therefore, based on the results of this study it is suggested that the presence of Cu at the Mn/SiO₂ interface during barrier layer growth does not inherently alter the chemical composition of the barrier layer formed following high temperature thermal annealing. Furthermore, it can be conclusively stated that the growth of Mn based barrier layers through the deposition of MnO_x/Cu alloys does not result in the growth of Mn oxide species within the barrier layer region. This result is in contrast with the findings of several publications within the literature;^{6,11} however, it should be noted that this discrepancy could be attributed to differences in the methods of sample fabrication and analysis. Nonetheless, due to the fully *in situ* growth and analysis experimental approach adopted in this study, it can now be stated that the presence of Cu at the Mn/SiO₂ interface during barrier layer growth does not result in the inherent growth of Mn oxide species within the interfacial region.

IV. CONCLUSIONS

The results of this study show that Mn silicate (MnSiO₃) barrier layers, with a thickness of ~2.6 nm, are chemically stable at elevated temperature in the presence of Cu. Using a fully *in situ* growth and analysis procedure x-ray photoelectron spectroscopy was used to monitor the chemical composition of a ~1 nm Cu layer deposited on the MnSiO₃ surface, with results showing no evidence for chemical interaction between the Cu and MnSiO₃ layers following thermal annealing up to 400 °C. This result is of considerable significance given that the formation of Cu oxide species is known to act as an intermediate step in the diffusion mechanism of Cu ions into silica based dielectrics. The effectiveness of MnSiO₃ as a barrier to Cu diffusion was also investigated using electron loss spectroscopy, with results indicating that MnSiO₃ is a barrier to Cu diffusion following thermal annealing to 400 °C. Section II of this study focused on

investigating the effect of Cu on the inherent chemical interactions which occur at the Mn/SiO₂ interface during barrier layer formation. Following the deposition of a ~2 nm MnO_x/Cu alloy, it was shown that thermal annealing results in the formation of a MnSiO₃ barrier layer, the chemical composition of which was identical to that formed in the absence of Cu. Importantly, results show no evidence for the formation of Mn oxide species within the barrier layer region following alloy deposition, which is in contrast with the results of previous publications. Based on the results of this study, it is suggested that Cu is chemically inert during the formation of MnSiO₃ layers on SiO₂ and the presence of Cu at the Mn/SiO₂ interface during Mn silicate growth does not inherently alter the chemical composition of the barrier layer. The 2011 ITRS roadmap¹⁹ suggests that a barrier thickness of <2 nm is required for future technologies, therefore, the results of this study suggest that MnSiO₃ may be a suitable candidate for integration into future generations of interconnects.

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