

Photoemission study of the SiO₂ conversion mechanism to magnesium silicate

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The objective of this work is to investigate interface chemistries which minimize the interfacial silicon oxide transition region at Si/high-*k* dielectric interfaces. We report on the mechanism by which a silicon native oxide layer is converted into magnesium silicate. The deposition of metal Mg onto a SiO₂ native oxide surface resulted in the formation of a magnesium silicide in addition to substoichiometric silicon oxides and a significant decrease in the oxidised silicon signal. Annealing to 300 °C resulted in the decomposition of the magnesium silicide, oxidation of the Mg, and the desorption of excess metallic Mg. Subsequent annealing to 500 °C resulted in converting the SiO₂ into magnesium silicate. The results suggest that the decomposition of the Mg silicide in the presence of the residual native oxide facilitates silicate formation at 500 °C. Due to the reported thermal stability of Mg silicate it is suggested that this process may be beneficial in modifying the interface characteristics of the Si/high-*k* dielectric interface which has potentially significant implications for future semiconductor device generations. © 2010 American Institute of Physics. [doi:10.1063/1.3357392]

I. INTRODUCTION

Controlling the interfacial properties of silicon is one of the biggest challenges facing the integration of high-*k* materials in future silicon based transistor technology. The thermal stability of the interfacial region must be addressed in order to prevent the growth of interfacial SiO₂, which can adversely affect the equivalent oxide thickness of the device.¹ The formation of thermally and chemically stable metal-silicates at the silicon surface may prevent the growth of SiO₂. Previous studies have shown that silicate layers can be formed by deposition of various metals including yttrium,² lanthanum,³ and erbium,⁴ and have been shown to produce promising electrical and physical characteristics. In this study the formation of a magnesium silicate interfacial layer is investigated as an alternative to SiO₂ due to its high reported thermal stability.⁵ Previous studies have shown that MgO deposition onto Si results in the growth of a thin (<1 nm) interfacial Mg silicate region.^{6,7} Further studies also indicate that these films lead to favorable interface characteristics including low interface state densities.⁸ However, it has also been reported that the strong tendency for MgO to crystallize results in the film displaying a high density of columnar grains within the oxide films, independent of growth method.^{9,10} The grain boundaries associated with these columnar structures may result in the rapid formation of breakdown paths, dramatically reducing the lifetime of the devices.¹¹ Therefore the focus of this work is to investigate the potential benefits of using magnesium silicate as a chemically stable interlayer between the silicon substrate and a high-*k* material in order to control the interfacial properties. The results suggest that it is possible to convert a SiO₂ native oxide layer into Mg silicate, and the mechanism by which

this occurs is discussed. Also, due to the thermal instability of Mg silicide, the formation of Mg silicate can be achieved *in situ* in ultrahigh vacuum (UHV) conditions. This allows for greater understanding of the reaction mechanisms involved in metal-silicate formation, specifically the role of silicide formation.

II. EXPERIMENTAL PROCEDURE

Si(111) native oxide surfaces were prepared using a standard degreasing procedure of successive dips in acetone, methanol, and isopropyl alcohol before being loaded into a UHV deposition and analysis system. Pure magnesium metal (99.9%) was deposited at room temperature at a pressure of 1×10^{-9} mbar onto the native oxide surface using thermal evaporation. The x-ray photoelectron spectroscopy (XPS) analysis was carried using a Vacuum Generator (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 analyzer 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 1×10^{-9} mbar, with samples kept at the target temperature for 20 min. Information on the species which desorbs from the surface during thermal annealing was acquired with Ametek process instruments—Dycor mass spectrometer, set to monitor atomic masses of 24 (Mg) and 40 (MgO). 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 2*p* substrate peak was 0.80 eV and the oxides, silicides, and silicate component peaks were in the range 1.2 to 1.5 eV. The corresponding O 1*s* core level spectra have FWHM values in the 1.75 to 1.9 eV range.

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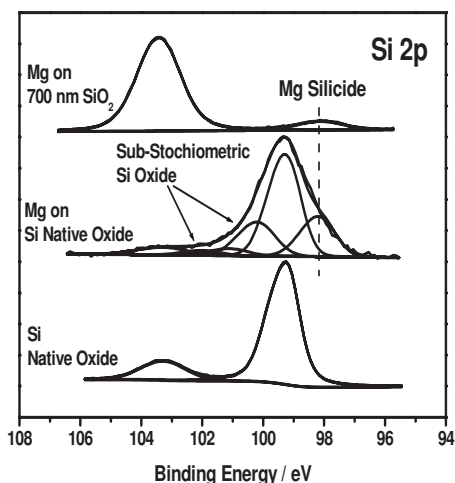


FIG. 1. Curve fitted Si $2p$ spectra showing the growth of Mg silicide and substoichiometric silicon oxide species after Mg deposition (2 nm) onto Si native oxide surfaces. The growth of Mg silicide on 700 nm SiO_2 surfaces suggests disruption of the SiO_2 structure resulting in Mg atoms taking the place of the O atoms.

All spectra were charge references to the Si $2p$ bulk signal at 99.3 eV and there was no evidence of differential charging effects for the native oxide covered surfaces.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The curve fitted Si $2p$ spectra taken from a SiO_2 native oxide covered silicon surface before and after ~ 2 nm Mg deposition, shown in Fig. 1, illustrate that Mg deposition has resulted in the growth of peaks on both the higher binding energy (HBE) and lower binding energy (LBE) sides of the Si bulk peak. The HBE peaks have been attributed to substoichiometric silicon oxide peaks which appear as the result of Mg incorporation within the SiO_2 layer. The LBE peak, separated from the Si substrate peak by 1.1 eV, has been attributed to the presence of magnesium silicide, which is consistent with the results reported by Brause *et al.*¹² The formation of a metal silicide resulting from the deposition of a reactive metal onto a thin silicon surface oxide is usually associated with a reaction between the metal and the silicon substrate. This is because the normal thermodynamic trend for metal oxides used as high- k dielectrics is that the metal oxide is thermodynamically more stable than the silicide. Therefore, depositing these metals on thin Si oxide layers usually results in the formation of a metal oxide by the reduction in SiO_2 ¹³ releasing silicon which can subsequently oxidize and contribute to the formation of an increased silicon oxide interlayer. In this case, the Mg preferentially reacts with the silicon atoms within the native oxide layer. This has been conclusively illustrated in a separate study where Mg was deposited on a SiO_2 layer of effectively infinite thickness (700 nm) and, as shown in Fig. 1, the metal silicide was clearly observed. However, interface reactions are not necessarily predictable from bulk thermodynamic data as the non-equilibrium nature of the deposition process can have an impact on interface composition^{14,15}

The growth of Mg silicide in the absence of bulk silicon suggests that the Mg atoms have disrupted the SiO_2 structure

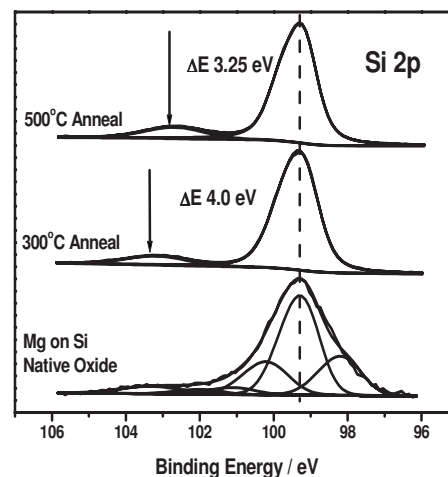


FIG. 2. Curve fitted Si $2p$ spectra taken after UHV annealing to 300 °C show the complete removal of Mg silicide and substoichiometric Si oxide species, along with a reduction in SiO_2 from 17% to 10% of the signal. Further annealing to 500 °C results in a chemical shift in the Si oxide peak, which is indicative of the transformation of SiO_2 to Mg silicate.

resulting in Mg atoms taking the place of the O atoms, creating Mg–Si bonds. Following the deposition of Mg on the native oxide surface, the samples were annealed in UHV to 300 °C and the changes in the Si $2p$ spectrum shown in Fig. 2 suggest the complete removal of Mg silicide, along with the removal of the Si suboxide groups. The thermal instability of Mg silicide has previously been reported.^{12,16} The reduction in the SiO_2 peak area from 17% to 10% of the total signal is consistent with the loss of oxygen from the surface during Mg silicide formation but there is no discernable shift in the peak position of the silicon oxide indicating that after this anneal, the silicon within the oxide is predominantly in the Si^{4+} oxidation state.

The Mg $2p$ spectrum in Fig. 3 relating to the deposition of Mg results in the appearance of an asymmetric peak indicative of metallic Mg.¹⁷ Annealing to 300 °C results in a 1.8 eV shift in the Mg $2p$ peak toward HBE, which is in-

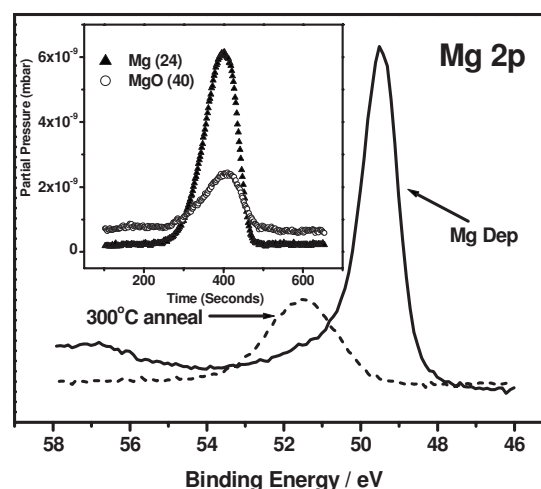


FIG. 3. Mg $2p$ spectra of the core level following Mg deposition and the subsequent 300 °C anneal which results in the oxidation of the Mg. A reduction in the integrated area of the peak by a factor of 2.5, along with mass spectrometry data (inset) suggest desorption of excess Mg from the surface during annealing.

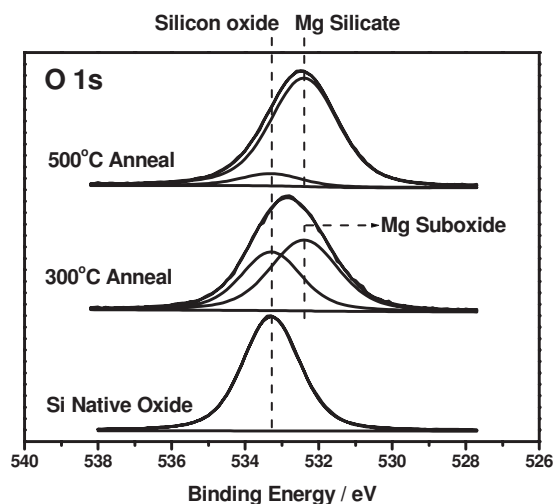


FIG. 4. Normalized O 1s core level spectra show the presence of both SiO₂ and partially oxidized Mg species after a 300 °C anneal. The reduction in the SiO₂ peak after a 500 °C anneal provides further evidence for the transformation of SiO₂ into Mg silicate.

indicative of the oxidation of the remaining Mg present on the SiO₂ surface. The integrated area under the Mg 2p peak was also reduced by a factor of 2.5 as a result of the anneal suggesting desorption of excess Mg from the surface. This is substantiated by mass spectrometry data taken during annealing, shown in the inset of Fig. 3, where the predominant species desorbing from the surface at 300 °C is Mg with a smaller contribution from MgO. The desorption of metallic Mg from the surface is in agreement with the work of Galkin *et al.*¹⁶ which suggest that room temperature deposition of Mg onto Si initially results in the formation of silicide islands while continued deposition results in the growth of metallic Mg on top of these island structures. Other studies¹⁸ have shown that metallic Mg will desorb from the Si surface at temperatures above 200 °C.

The changes induced in the Si 2p peak profile in Fig. 2 after subsequent annealing of the sample to 500 °C results in a significant shift in the Si oxide peak. The Si oxide peak now shows a separation from the bulk peak equal to 3.25 eV, which is indicative of Mg silicate and not SiO₂. The peak position of Mg silicate with respect to the silicon substrate peak has previously been found during MgO deposition onto the Si(111) surface,⁷ and verified using Mg silicate reference materials. Peak fitting of the Si 2p spectrum in Fig. 2 suggests that the contribution of the Si⁴⁺ oxidation state has been reduced below the level of detection for standard XPS, which indicates a considerable reduction in the presence of the SiO₂ native oxide. Mg 2p spectra (not shown) taken after the 500 °C anneal show a 0.2 eV shift to LBE, which is consistent with Mg silicate formation. It should also be noted that there is no discernable change in Mg 2p peak area, indicating that the oxidized Mg formed after at 300 °C annealing does not desorb during the 500 °C anneal.

Further evidence that the SiO₂ native oxide has been converted into Mg silicate comes from the evolution of the O 1s spectrum illustrated in Fig. 4. The deposition of Mg on the SiO₂ native oxide surface leaves the O 1s peak profile unchanged which supports observations from the Si 2p core

level that the room temperature interaction of Mg with the SiO₂ occurs preferentially with the silicon atoms in the SiO₂. Curve fitting of the broadened O 1s peak observed after 300 °C annealing reveals the presence of an oxidized Mg component shifted by 1.0 eV to LBE in addition to the SiO₂ peak, which is consistent with the oxidation shown in the Mg 2p profile. This energy separation between the two oxide components of the O 1s spectrum is less than that seen between SiO₂ and fully stoichiometric MgO, which has been measured in separate experiments to be 1.54 eV. Therefore, although the Mg is in an oxidized state, it is not in the fully oxidized species MgO. It can also be said that the Mg atoms are not in a silicate bonding environment as the silicon oxide state shown in the Si 2p spectra (Fig. 2) is still indicative of the SiO₂ native oxide. After annealing to 500 °C there is a significant decrease in the presence of the SiO₂ related component within the O 1s core level profile. Given that there is no change in the total integrated area of the peak, this again indicates that the SiO₂ has been converted into Mg silicate consistent with the observations on the Si 2p core level. While the Mg 2p core level spectrum shifts by 0.2 eV between the suboxidized Mg and the Mg silicate, no corresponding binding energy shift is observed between the Mg suboxide and Mg silicate components of the O 1s spectra. This would indicate that the binding energy position of the O 1s spectrum is insensitive to chemical changes between oxidized magnesium and magnesium silicate. The chemical shifts shown by the Si 2p, Mg 2p, and O 1s spectra after Mg silicate formation are in accordance with the electronegativities of magnesium, silicon, and oxygen (1.31, 1.90, and 3.44 on the Pauling scale). These values would also suggest that the O 1s binding energy position of both suboxidized magnesium and magnesium silicate would exist between the SiO₂ (BE=533.3 eV) and MgO (BE=531.8 eV) which agrees with the above observations. Subsequent studies have shown that the determining factor in silicate growth is the amount of Mg silicide initially formed on the SiO₂ surface. The importance of silicide formation as an intermediate step to silicate formation has previously been suggested by Chambers and Parsons² and can be conclusively shown here. The spectra in Fig. 1 showed the effect of ~2 nm Mg deposition on to SiO₂, which caused the growth of Mg-silicide and eventually led to the growth of Mg silicate. However, if only 1 nm of Mg is deposited, an insufficient amount of Mg silicide is formed, and annealing to 500 °C results in only partial transformation of the SiO₂ into Mg silicate as can be seen in the Si 2p spectra in Fig. 5.

Further evidence for the importance of silicide formation comes from analyzing the chemical species present on the surface after annealing to 300 °C. The Si 2p spectrum in Fig. 2 taken after the 300 °C anneal shows no evidence of Mg-silicide, while the silicon oxide present on the surface remains in the form of SiO₂. Also, Fig. 3 shows that the Mg present on the surface after the 300 °C anneal is in the form of oxidized Mg, but not fully oxidized MgO. Therefore, while the only chemical species present are oxidized Mg and SiO₂, annealing the sample to 500 °C still results in silicate formation. This is in direct contrast to the result seen after the deposition of stoichiometric MgO onto the SiO₂ native

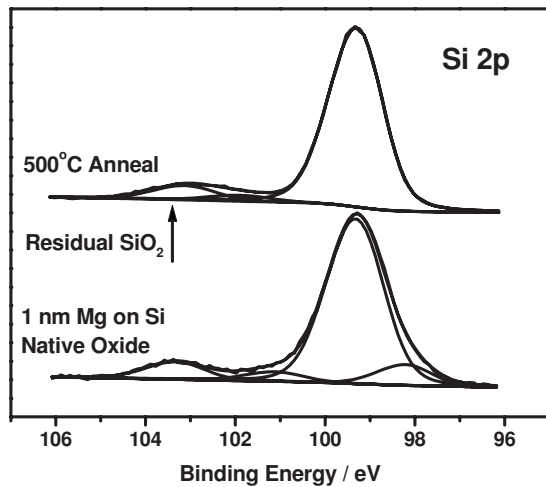


FIG. 5. Si 2p spectra taken after 1 nm Mg deposition onto Si native oxide surface show the growth of less Mg silicide than that seen in Fig. 1. Subsequent UHV annealing to 500 °C resulted in only partial transformation of SiO₂ into Mg silicate, indicating the importance of silicide formation as an intermediate step in Mg silicate growth.

oxide surface (not shown) where the spectra taken after annealing to 500 °C show no evidence for the transformation of SiO₂ into Mg silicate. This would indicate that the presence of SiO₂ and stoichiometric MgO will not lead to silicate formation at 500 °C without the effect of the intermediate silicide formation at room temperature and subsequent decomposition at 300 °C prior to the 500 °C anneal.

Given the importance of silicide in silicate formation, it is suggested that the thermal instability of Mg-silicide offers an advantage over other metal-silicides. The thermal removal of Mg silicide prior to Mg silicate formation is in contrast to the silicide oxidation process developed for the formation of other metal silicates such as Y silicate^{2,19} and Hf silicate.²⁰ Previous studies have shown that the oxidation of Y silicide can only be achieved at high temperature (600°–900 °C) and high pressures of N₂O (1 atm), while high pressure ozone oxidation has been used to form hafnium silicate from deposited hafnium silicide. The presence of excess oxygen in the high temperature annealing of rare earth silicates has been shown to result in the growth of interfacial Si–O–Si bonds.²¹ However, it should also be noted from our studies that the desorption of excess metallic Mg from the silicon surface at 300 °C means that it is difficult to promote additional silicide formation above that which forms initially at room temperature. The thermal instability of Mg silicide therefore means that only those Si atoms which are involved in silicide formation after Mg deposition can be incorporated into Mg silicate, placing a limit on the achievable thickness of the silicate film. This contrasts with the experimental observations reported by Baglin *et al.*²² for the promotion of yttrium silicide growth at elevated temperature.

The results of this study may have relevance for the low temperature modification of silicon interlayers on III-V materials which have been deposited prior to high-*k* dielectric deposition, in an attempt to improve the interfacial electrical characteristics.²³ While Jiang *et al.*²⁴ have shown that thin amorphous silicon interlayers can be successfully converted

into ytterbium silicide, high temperature annealing could detrimentally impact on the interface quality as III-V materials are unstable at high temperature.²⁵ The Mg silicate formation procedure at 500 °C outlined in this work may make it more suitable for silicon interlayer modification on III-V semiconductor substrates than other metal silicates.

IV. CONCLUSIONS

The results presented here suggest that a SiO₂ native oxide layer can be converted into Mg silicate. Initial deposition of Mg onto the SiO₂ surface resulted in the growth of Mg silicide due to disruption of the SiO₂ and loss of oxygen from the surface. Annealing the sample to 300 °C resulted in removing the thermally unstable Mg silicide and desorption of excess Mg from the surface. It is believed that the decomposition of Mg silicide creates under coordinated silicon atoms which react with the oxidised Mg resulting in the formation of Mg silicate upon annealing to 500 °C. The study has also shown that the initial formation of Mg silicide is a necessary intermediate step in Mg silicate growth and can only be achieved by deposition of metallic Mg.

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