Investigating the Efficacy of Hafnium Dioxide Barrier Layers to Halt Copper Oxide Formation in Redistribution Layers for Three-dimensional (3D) Packaging

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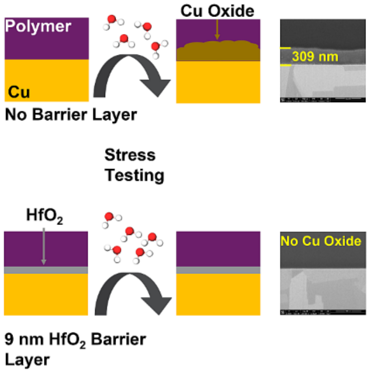
Abstract

HfO_2 is investigated for its suitability to act as an oxygen and moisture barrier to prevent Cu oxidation in redistribution layers (RDLs) in 3D packaging technologies. Different thicknesses of the HfO_2 barrier were deposited via atomic layer deposition (ALD) on Cu surfaces and then stressed by (i) high temperature stress and (ii) humidity and thermal stress for 1000 hours to ascertain the optimal thickness to prevent oxidation of the Cu. Thickness of the ALD HfO_2 film was monitored by ellipsometry, while the extent of Cu oxidation was monitored by FIB (focus ion beam) prepared SEM cross sections. It is found that ~9 nm of HfO_2 is sufficient to prevent Cu oxidation.

TOC GRAPHICS



KEYWORDS Low temperature atomic layer deposition, 3D packaging technologies, polymer based RDLs, stress testing, copper oxide

With the continued evolution of nanoelectronics beyond Moore's Law, into areas such as the Internet of Things (IoT), artificial intelligence (AI) and wearable technology, industry must find new ways to deliver improved devices. Consumers are interested in more energy efficient devices that have a low power consumption, are faster and that have additional features compared to previous generations. Heterogenous integration achieved through advanced 3D packaging technologies is seen as the next paradigm to realize these technologies.[1–3] In 3D architecture different electronic components are placed directly on top of each other in a vertically stacked arrangement. They are then connected by a series of metal redistribution layers which act to reroute the signal from the device to the packaging level.[4–6] The Cu in these RDLs can suffer from problems like Cu diffusion, electromigration and oxide formation due to the hygroscopic nature of the surrounding insulating polymer, for this reason solutions are required to protect the Cu.

Previous work by Chery *et. al.*[7] exhibits the need for a barrier or capping layer on top of the metal line before subsequent spin coating of the next polymer layer. It was observed how different stresses could lead to the formation of Cu oxide which was due to the polymer insulator absorbing oxygen and water during these stress tests. Moreau *et. al.*[8] were also able to demonstrate how using inorganic (SiN, SiO_2) layers and organic/inorganic (fluoropolymer and Ni) bilayers as passivation layers, could halt corrosion of the Cu RDLs and stop Cu oxide formation. Although, from their SEM images their passivation layers appear to be quite thick (no thickness is specified in the text) possibly > 100 nm. However, their study is vitally important as it shows that passivation layers or barrier layers can be used to stop Cu oxide forming. To make this approach attractive for implementation into the fabrication process, the barrier thickness needs to be kept to a minimum and materials with compatible etch chemistries must be used. Li et al. summarize the industry standard for moisture/oxygen barrier layers used in organic light emitting diodes (OLEDs).[9] To form an effective moisture barrier, thickness of 50 nm or greater are needed with materials such as Al_2O_3, TiO_2 and ZrO_2. If a barrier is applied after the first metallization step, it is imperative that it does not create an etch stop where subsequent photolithography steps cannot proceed or have wildly different etch rates than the surrounding polymer. Low process temperature is another crucial requirement in RDLs therefore any barrier material must be capable of being deposited at lower temperatures. Temperatures below 200 °C are generally targeted although, the temperature used for the process will depend on the polymer itself. This is to avoid going above the glass transition temperature of the polymer which could induce extra mechanical stress leading to cracking thus rendering the device useless[10]. This condition excludes many relevant materials like TaN[11], Mn[12] and Ru[13] which are popular barrier layer and liner materials in interconnects, as they can only be deposited at higher processing temperatures. Chase et al. have successfully demonstrated that an Al_2O_3 barrier at thicknesses from 10 nm to 17 nm can block copper oxide formation for up to 216 hours of stress testing.[14] However, their process is performed at 200°C which is generally the upper limit for most polymers.

In this work, the RDLs are Cu lines surrounded by a thermoset phenol-based photosensitive polymer. HfO_2 was chosen as the barrier material as it has previously been shown to be an effective Cu diffusion barrier layer for interconnect applications, at a thickness as low as 3 nm.[15] In a CuHf alloy it has been shown to form HfO_2 at the top interface while protecting the Cu from oxidizing even during high temperature anneal in an oxygen atmosphere.[16] Thick HfO_2 films ~ 50 nm have also been shown to protect Cu against corrosion.[17] HfO_2 is also compatible with nanoelectronic fabrication and can be easily introduced into the RDL processing. Atomic layer deposition (ALD) is utilized to deposit the HfO_2 layers as it can deposit very uniform films at low temperatures and is widely used in large scale manufacturing of nanoelectronics. TDMAHf was employed as the Hf

ALD precursor since it has been shown to deposit Hf nitride films at substrate temperatures as low as 100 °C via ALD[18]. The aim of this work is to demonstrate how a thin HfO_2 barrier layer can prevent the Cu in the RDLs from becoming oxidized. To the best of the authors knowledge, this work demonstrates for the first time how an ultrathin 9 nm HfO_2 barrier layer is sufficient to block the oxidation of the Cu. It is shown how smooth conformal HfO_2 films can be deposited at temperatures as low as 100°C from a TDMAHf precursor. The ability of the HfO_2 to act as an oxygen and moisture barrier is demonstrated for a completely new materials system, namely the phenol-based polymer and Cu.

ALD was performed on blanket Cu substrates with various cycle numbers, from 10 ALD cycles up to 120 ALD cycles, creating samples of varying thicknesses. This was to ascertain the optimal thickness required to prevent Cu oxidation. The cycle sequence consisted of TDMAHf/N_2 purge/water/N_2 purge for 0.3 s/10 s/0.75 s/10 s at a substrate temperature of 100 °C. A reference Si sample was also present to compare the growth per cycle (GPC) with the Cu substrate. From Figure 1 (a) the GPC for both the Si and Cu substrates are the same after 120 cycles at 0.15 nm per cycle. Even at this low temperature process (100 °C) there is significant HfO_2 growth with ~ 18.5 nm deposited after the 120 cycles.

AFM images displayed in Figures 1 (b) and (c) exhibit the Cu before and after HfO_2 ALD using a scan size of 5 µm x 5 µm. For blanket Cu samples after a CMP step, the AFM, Figure 1 (b), reveals a smooth featureless surface with a roughness of ~ 1.1 nm. Although, some abrasions are noticed due to the CMP step. Following 120 cycles of ALD (Figure 1 (c)) it is observed that the surface morphology has changed, with an extensive grain structure from the deposited HfO_2 layer, where the z scale has been slightly increased for clarity. Even with the grain structure visible on the surface, the overall roughness has not changed from the initial Cu surface. A roughness profile displayed in Figure 1 (d) taken from the diagonal line (corner to alternate corner), verifies the conformality of the HfO_2 layer, which is the characteristic trait of ALD.

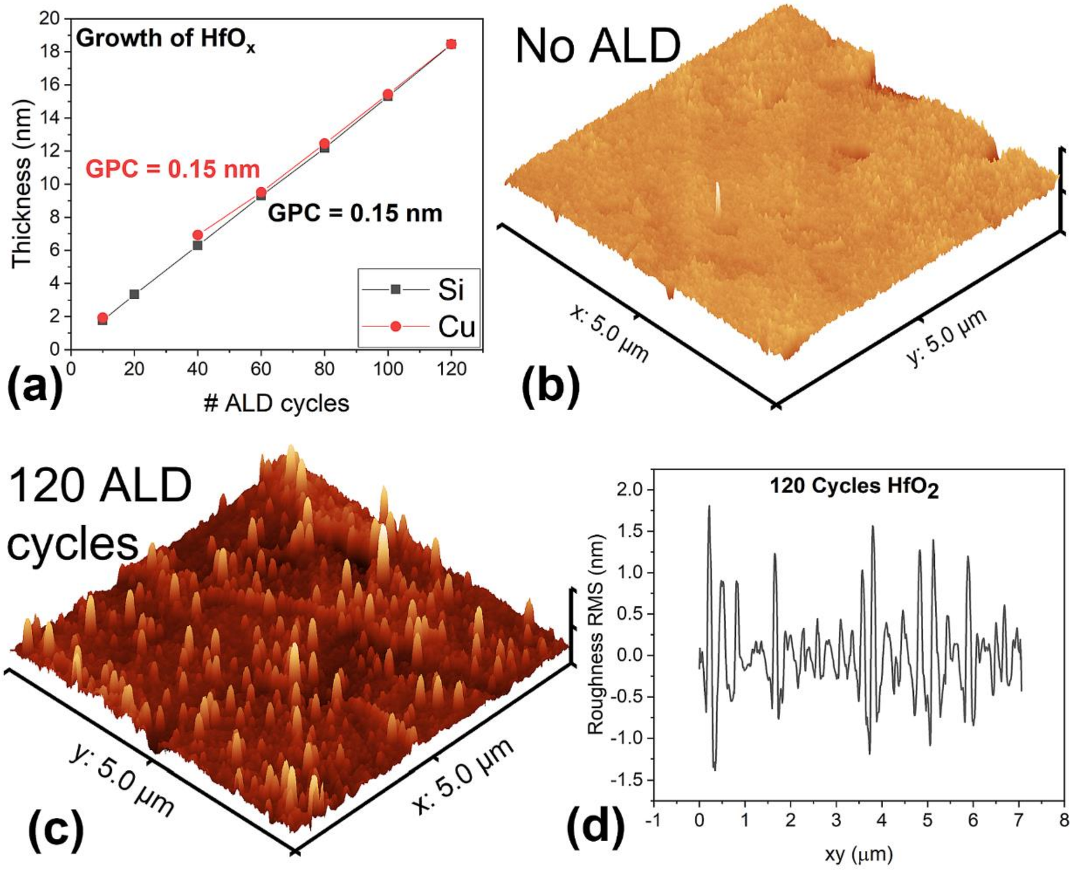


Figure 1 (a) displays the growth per cycle of the HfO_2 deposited on both Cu and Si samples at 100 °C, (b) AFM image of the Cu after CMP step and before any ALD, (c) AFM image after 120 ALD cycles showing the grain structure of the HfO_2 film and (d) roughness profile of the deposited HfO_2 film, taken from the diagonal going from left to right.

Subsequent to ALD, the samples were spin-coated with a layer of the polymer and then subjected to reliability testing via two different stress tests. These tests have been designed to drive oxidation of the Cu so we can assess and then pinpoint the mechanisms which lead to the failure of devices. The first stress test is a high temperature storage (HTS) which involves placing the samples in an oven at 150 °C for 1000 hours. A nitrogen rich atmosphere is maintained in the oven although ~ 2 % of oxygen is present during the process. This stress test is designed to initiate Cu diffusion into the surrounding polymer as well as causing the polymer to age prematurely. It has previously been shown that in an unprotected Cu line, a thick ~ 330 nm layer of Cu oxide is formed after the HTS.[7] Figure 2 shows the SEM images from FIB cross sections for 20, 40 and 60 ALD cycles on CMP Cu samples. In Figure 2 (a) 20 HfO_2 ALD cycles, which corresponds to ~ 3.6 nm of HfO_2, are not sufficient to protect the Cu. Clearly visible is a ~ 309 nm layer of Cu oxide which has formed as a result of the HTS testing. Although the sample which received 40 HfO_2 ALD cycles (~ 6.9 nm HfO_2 barrier) does perform better, a ~ 60 nm Cu oxide film is still observed, Figure 2 (b). Interestingly, in Figure 2 (c) 60 ALD cycles is sufficient to protect the Cu from oxidation. 60 ALD cycles deposits ~ 9 nm of HfO_2 and this film halts the diffusion of the moisture and oxygen into the underlying Cu preventing an oxide layer from forming.

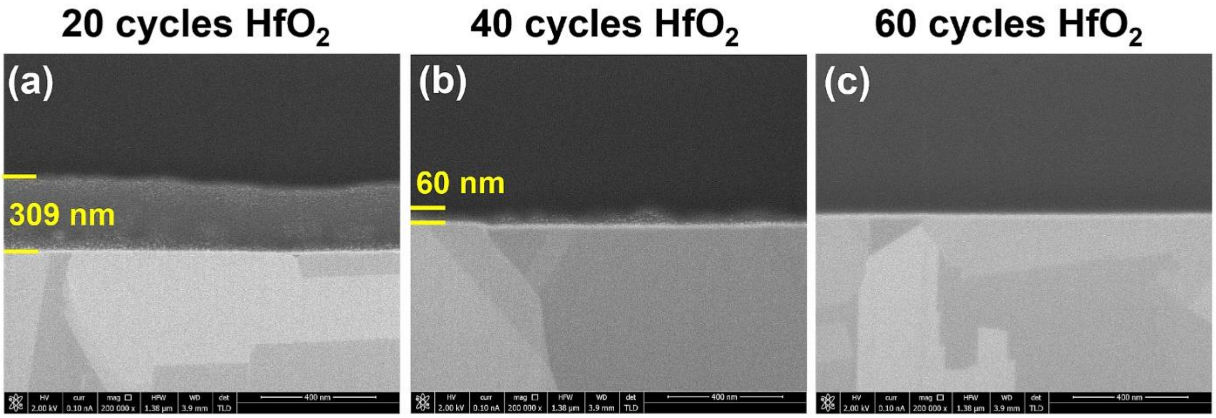


Figure 2 FIB cross sections of Cu samples, taken after HTS showing thick Cu oxide formation after (a) 20 HfO_2 ALD cycles, (b) 40 cycles and no oxide growth after (c) 60 cycles of ALD.

The second stress test performed was a corrosion stress test. Here the samples were initially subjected to 1000 hours at 85 °C in 85 % relative humidity. This test is designed to not just cause oxidation but to encourage moisture to diffuse through the polymer and interact with the HfO_2

layer. The samples are subsequently exposed to HTS performed at 150 °C for 1000 hours. This is an extreme stress test to assess the efficacy of our HfO_2 barrier layer. Figure 3(a), (b), and (c) display CMP Cu samples that have received 20, 40 and 60 ALD cycles, respectively. The same trend is observed for these samples as with the previous ones, a thick 356 nm Cu oxide film is seen when only 20 ALD cycles were performed. Following 40 ALD cycles a 204 nm Cu oxide film develops. This oxide is much thicker than in the previous stress test with the same number of cycles, showing just how extreme this stress test is. While again it is seen that 60 ALD cycles of HfO_2 are enough to prevent Cu oxide formation.

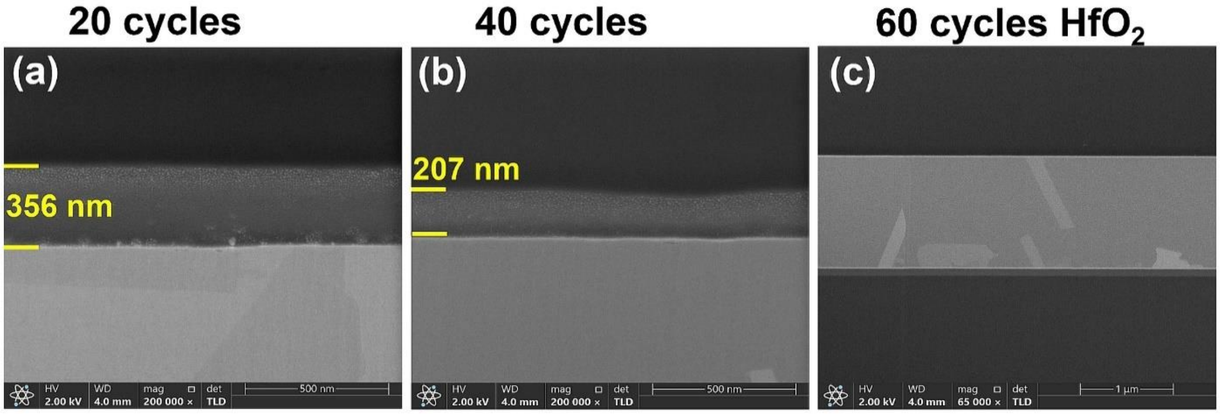


Figure 3 FIB cross sections of CMP Cu samples taken after TH stress showing thick Cu oxide formation after (a) 20 HfO_2 ALD cycles, (b) 40 cycles and no oxide growth after (c) 60 cycles of ALD. Due to technical error, the magnification for the 60 cycles sample is different to the others.

In conclusion, we have developed a process whereby a HfO_2 film can act as a barrier layer to prevent moisture and oxygen present in a polymer film from oxidizing the underlying Cu layer. By taking advantage of the low deposition temperature of the Hf ALD precursor the process will minimize any extra mechanical or thermal induce stress on the polymer. It has been shown that the HfO_2 has a steady growth per cycle during ALD and this is seen on both Si and Cu substrates. Most importantly we have demonstrated that a 9 nm HfO_2 barrier layer is sufficient to stop Cu oxidation in polymer based RDLs. To the best of our knowledge, this is one of the thinnest reported barrier layers used to stop Cu oxidation in RDLs. Going forward we would like to reduce the barrier thickness even further and test the efficacy of an 8 nm barrier. There is also the possibility to test other materials as a barrier layer.

EXPERIMENTAL METHODS

300 mm Si wafers were used as the starting substrates for this work. A Ta seed layer was grown on a 100 nm SiO_2 film. The Cu was electroplated and then received a chemical mechanical polishing (CMP) step to reduce its thickness to 1.5 µm and to leave a smooth surface. The Cu was stored in a nitrogen filled glove box to stop oxidation of the film. When needed, the Cu wafer was then cleaved into smaller coupon sized samples (3 cm x 3 cm) which were used immediately. ALD was performed in a Veeco Savannah S300 system. HfO_2 was deposited from a tetrakis(dimethylamido) hafnium (TDMAHf) precursor with water as a co-reactant. The cycle was as follows TDMAHf/purge/water/purge for 0.3 s/10 s/0.75 s/10 s. The substrate temperature was maintained at 100 °C, while the precursor was heated to 75 °C and the water was maintained at 30 °C. Different cycle numbers were performed to get samples of varying thicknesses, from 10 ALD cycles up to 120 ALD cycles. Thickness of the HfO_2 overlayer were measured on a J. A. Woollam RC2 Spectroscopic Ellipsometer at three different incident angles, 65°, 70° and 75° with a 5 s acquisition time at each angle. A standard Cauchy model was used to fit the data.

Following HfO_2 ALD a layer of the photosensitive phenol-based polymer manufactured by JSR Corporation was spin coated onto the samples and cured. The samples were then subjected to the different stress tests. The high temperature stress tests were carried out in a Thermo Scientific Heraeus UT6060 oven. This oven is capable of maintaining a nitrogen atmosphere. The temperature humidity stress tests were carried out in a climate chamber Weiss SB22.

High resolution images were taken through cross-sections of the partly oxidized copper lines by focused ion beam (FIB) milling using a FEI Helios Dual Beam system.

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Notes

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The authors declare no competing financial interests.

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