Role of Bath Composition in Electroless Cu Seeding on Co Liner for through-Si Vias

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To enable Cu fill of through-Si vias (TSV) with a high aspect ratio (diameter 3 μm, depth 50 μm), the electroless deposition of a Cu seed on Co liner material was investigated. The reducing agent glyoxylic acid showed anodic oxidation on Co, which did not appear for the case of formaldehyde. From electrochemical analysis, an optimized bath composition caused limited Co corrosion during the electroless Cu nucleation phase. The concentration ratio of the complexing agent (ethylenediaminetetraacetic acid) and copper was found to strongly impact the liner corrosion; in case free complexing agent is present in the bath, the Co corrosion was assisted by complexion and replacement reactions. A continuous seed layer could be deposited in the entire TSV, which enabled the filling by electrochemical deposition (ECD). The substantially thinner total copper overburden generated for this combination of a wet-chemical seed deposition and an ECD fill process contributes to a cost reduction of its chemical mechanical polishing (CMP). Without liner, as well as its material costs, can have an impact on the total costs for processing.18 In alkaline ECD Cu has been investigated for direct Cu plating on a Co liner.19,20 In alkaline solution, the Cu forms a passivation layer, i.e., Cu(OH)2, and this passivated Co is less prone to corrosion compared to the situation where the Co is exposed to an acidic plating solution.21 Even an electrodeposition process in alkaline solution still faces challenges when the Co liner thickness is to be scaled further because terminal effects will come into play during the ECD process and this introduces thickness variations across the wafer. For an electroless seeding process on a liner, there is no need to consider the terminal effect because no external current is applied (the deposited Cu seed layer should be sufficiently thick to facilitate a good deposition uniformity for the subsequent ECD filling step). In addition, ELD Cu can also be performed in the alkaline pH range as long as the reducing agent is active. Furthermore, compared to a seed deposited by PVD, an electroless seeding process eventually yields a thinner total Cu overburden, which is to be removed by CMP.19

In this paper, we investigate the electrochemical reactions involved in ELD Cu from an alkaline solution to obtain more understanding of the impact of the bath composition for generation of a wet seed on a Co liner inside 3 μm diameter and 50 μm deep TSVs.

Experimental

For the electrochemical measurements, a stack consisting of CVD-Co (30 nm) / ALD-TiN (12 nm) / SiO2 (100 nm) / Si was used as substrate. On patterned samples with TSVs having a 3 μm circular opening and 50 μm depth, a CVD-Co film with a nominal thickness of 45 nm was deposited on the aforementioned stack. The ELD Cu solution contained 0.03 mol/L copper sulfate as Cu ion source and 0.03 or 0.18 mol/L ethylenediaminetetraacetic acid (EDTA) as a complexing agent. As stabilizer and brightener, 40 ppm of 2,2′-bipyridyl was added to the Cu-EDTA solution. The pH of the Cu-EDTA solution and the ELD bath was maintained to 12.5 using tetramethylammonium hydroxide (TMAH; Fujifilm, Silicon Etch #933979). From separate solutions, 0.2 mol/L glyoxylic acid or formaldehyde as a reducing agent and 500 ppm of polyethylene glycol (PEG Mw 4,000) were added. Mixed potential measurements were done using a rotation disc electrode system at 50 RPM. Cross-sectional transmission
Results and Discussion

To continuously deposit a metal at a target thickness using an electroless process, a self-catalyst reaction of reducing agent on the plated metal is required. In case the metal which needs to be plated and the substrate metal are different, the nucleation of the ELD requires the anodic oxidation of reducing agent on the substrate metal to be possible. Additionally, if the metal liner is less noble than Cu, the replacement reaction of the liner has to be considered. For the latter, the liner film thickness decreases, a process which needs to be well-controlled (and preferably avoided), to ensure sufficient liner remains at the bottom of high aspect ratio features. Such an interplay with the Co replacement reaction can also give a ‘driving force’ to nucleate the metal deposition.19 During the initial stage of Cu film growth on a Co liner, a competition can occur between the replacement and deposition reaction. Therefore, the ideal ELD Cu solution needs to contain a reducing agent that shows anodic oxidation both on the Co liner as well as on Cu, and it should exhibit a minimal replacement reaction. To understand the nucleation mechanism and investigate the surface reactions involved, electrochemical measurements are required.

Anodic oxidation of the reducing agent on Co.— Ohno et al. evaluated the possibility of anodic oxidation of reducing agents on different metal electrodes.20 From their results, formaldehyde is a suitable reducing agent for ELD Cu as it shows anodic oxidation on a copper electrode, which indicates the ability of self-catalyst reduction of Cu. However, when formaldehyde was used as a reducing agent to deposit Cu on a Co liner, it did not show anodic oxidation on Co. This means that the Cu nucleation on Co can solely be a replacement reaction. Another candidate of reducing agent for the self-catalytic reaction of Cu is glyoxylic acid.21–25 Yu et al. reported on the anodic oxidation of glyoxylic acid on Cu.26 In addition, in our previous study, it was clarified that glyoxylic acid can show anodic oxidation on both Cu and Ru.26

Figure 1 shows linear sweep voltammograms of glyoxylic acid and formaldehyde for a 30 nm Co liner. For the case of formaldehyde, anodic oxidation was absent in the range from −0.65 to −0.45 V, which is the potential range in which the reducing agent should be active to lead to reduction of the Cu-EDTA complex.27,28 Our result for formaldehyde is very similar to the results of Ohno et al.,20 which means that formaldehyde cannot be used as reducing agent on Co surfaces. On the other hand, glyoxylic acid shows anodic oxidation on Co in the voltage range of −0.65 to −0.45 V (Figure 1). The cathodic process in the range from −1 to −0.9 V is attributed to the reduction of water to hydrogen. The plateau around −0.9 to −0.7 V is ascribed to the reduction of dissolved oxygen (the solution was not degassed). In recent work, we found that the glyoxylic acid oxidation on Ru is impacted by dissolved oxygen.29 Therefore, removing the oxygen by N2 bubbling and/or deposition in an inert atmosphere could increase the reactivity of the reducing agent for the ELD process.29

Cathodic reaction of Cu complex on Co.— For a self-catalyst electroless process, both reducing agent and complexed Cu ions should be present. In the case of glyoxylic acid, the pH range where it can be an effective reducing agent was found to be between 12 and 13.21 If no complexing agent is present, copper ions form Cu hydroxide when the pH is above 5. Therefore, a suitable complexing agent should be added to maintain a thermodynamically stable bath. A frequently used complexing agent is EDTA because of its high stability constant with Cu ion (Cu(EDTA)2−; pKstab = 18.80).30

Figure 2 shows open-circuit potential (OCP) transients for a Co substrate immersed in a Cu-EDTA solution containing 2.2′-bipyridyl as stabilizer. Here, the concentration ratio (CR) denotes the ratio of EDTA to Cu molarity. When there is no free EDTA in the solution (CR = 1), the transient remains essentially unaltered for 1200 sec. In case of an excess of EDTA (CR = 6), the potential starts around −0.6 V. After 600 sec, the potential gradually increases and levels off to −0.2 V at about 900 sec. The dashed line in Figure 2 shows a potential transient of EDTA only which has similarities with the curve of an EDTA excess in the solution (CR = 6). In this case, however, the onset of the potential increase to −0.2 V is seen at 600 sec. In both solutions, the increase in the OCP is believed to be related to the Co corrosion as will be discussed below.

The corrosion process was studied by measuring linear sweep voltammograms after immersion of the Co either into an EDTA only or a Cu-EDTA solution for a certain timeframe during which the system was left at OCP (see Figure 3a and 3b). For both solutions, the initial amount of free EDTA is the same (0.15 M). By measuring a series of voltammograms, the transient processes at the surface were monitored (a fresh sample was used for each voltammogram).

The potential of Figure 3a was swept from OCP into positive direction. An anodic stripping current peak appears for an immersion time of 5 sec, which becomes smaller when the sample is immersed for longer times (for an immersion time of 600 sec the peak was absent). The transient process at OCP can, therefore, be attributed to the adsorption of EDTA on the Co surface and the formation of a stable Co(EDTA)2− complex in the electroless bath (pKstab = 16.45).31 This confirms that the change in the open-circuit potential measurements

Figure 1. Polarization analysis of 0.2 M of glyoxylic acid and formaldehyde on a Co surface. Conditions: 40°C, scan rate 2 mV/sec.

Figure 2. Open-circuit potential transients for different EDTA concentrations in Cu-EDTA solutions and 0.15 M EDTA solution on 30 nm Co. The concentration ratio (CR) refers to [EDTA]/[Cu] for which [Cu] = 0.03 M for all cases. Conditions: 40°C, pH 12.5.
In this experiment, the Co thin film was used is possible to electrodeposit Cu on Co in absence of free EDTA. For oxide can occur, i.e. some contribution to the cathodic current measured down to $0.4 \text{ V}$ is present due to dissolved oxygen. Overall, Figure 4 shows it down to $0.5 \text{ V}$ gradually decreases as a function of time to qualitatively understand the surface reactions on the Cu layer. The trend of the voltammograms for different immersion times in Figure 3b can be explained as the following. Initially, there is a replacement reaction between Co and the Cu-EDTA leading to Cu deposition on the Co liner. This replacement reaction is the only way to deposit Cu in this particular bath because a reducing agent is left out on purpose for these measurements. This Cu-on-Co replacement reaction leads to a mixed composition of the surface and, hence, two peaks appear during the anodic dissolution (‘stripping’) of this stack. Once the Co surface is fully covered by Cu, the replacement reaction ceases and this self-limited reaction is visualized as a decrease in the peak area (range from $-0.5 \text{ to } -0.3 \text{ V}$ increases as a function of the immersion time. This is attributed to anodic dissolution of the Cu which was deposited on the Co liner at OCP. For an immersion time of 300 and 600 sec, the maximum current of this peak is similar, while for an immersion time of 900 sec, both peaks have disappeared.

The trend of the voltammograms for different immersion times in Figure 3b can be explained as the following. Initially, there is a replacement reaction between Co and the Cu-EDTA leading to Cu deposition on the Co liner. This replacement reaction is the only way to deposit Cu in this particular bath because a reducing agent is left out on purpose for these measurements. This Cu-on-Co replacement reaction leads to a mixed composition of the surface and, hence, two peaks appear during the anodic dissolution (‘stripping’) of this stack. Once the Co surface is fully covered by Cu, the replacement reaction ceases and this self-limited reaction is visualized as a decrease in the peak area (range from $-0.6 \text{ to } -0.5 \text{ V}$ for the anodic stripping of the stack. Furthermore, when the Cu layer is fully closed, it cannot grow in thickness and the peak in the range from $-0.5 \text{ to } -0.3 \text{ V}$ remains unaltered (compare the 300 sec and 600 sec curves). Eventually, both metals are dissolved by the complexation of free EDTA, which can explain the absence of a peak in the voltammogram started after 900 s immersion time.

In order to understand in more detail what happens in the Cu electroless bath when there is no free EDTA present, electrochemical measurements were done using a Cu-EDTA solution (CR = 1). A cathodic voltammogram and OCP transient of this solution are shown in Figure 4 and 5, respectively. The voltammogram, which was started from the OCP, shows exactly what is expected from this solution. It starts with the Cu electrodeposition on the Co surface due to the applied potential and this is visualized with the reduction peak in the range from $-0.6 \text{ to } -0.7 \text{ V}$. After this, the water reduction is visible down to $-1.1 \text{ V}$. In the reverse scan, a small plateau around $-0.7 \text{ to } -0.4 \text{ V}$ is present due to dissolved oxygen. Overall, Figure 4 shows it is possible to electrodeposit Cu on Co in absence of free EDTA. For this experiment, the Cu thin film was used without any pretreatment to remove native oxide. Therefore, electrochemical reduction of cobalt oxide can occur, i.e. some contribution to the cathodic current measured may be present (no dedicated experiments have been performed to exclude this possibility). Additionally, an alkaline solution can lead to surface (hydr)oxide.

Now that the impact of the presence of EDTA on the Co liner corrosion is qualitatively understood, a reducing agent is added to the Cu solution making it an electroless bath. This Cu seeding is studied as function of time to qualitatively understand the surface reactions on the Co liner. Note that for the Cu-EDTA bath without glyoxylic acid the OCP remains unaltered in this timeframe (see Figure 2). Figure 5 shows the mixed potential transient of the glyoxylic acid based ELD Cu without free EDTA (CR = 1) on the primary axis, together with the Cu sheet resistance of the sample (secondary axis). The mixed potential of this bath has three phases in the first 600 seconds. During the first 30 seconds, the potential changes from $-0.45 \text{ to } -0.6 \text{ V}$ and refers to the induction time of the Cu electroless reaction. Once the glyoxylic acid becomes active on Co, the potential goes more negative due to Cu nucleation on Co. This was also found for other metal surfaces such as Ru and Pt. The induction time of the reaction is also visualized as a fairly constant Rs value for the Cu film. From 30 sec. to 300 sec., the potential decreases with about 50 mV. This part of the transient shows the Cu nucleation, which is also supported by the decrease in the Rs value from $\sim 500 \Omega \text{cm}^2 \text{ to } \sim 5 \Omega \text{cm}^2 \text{. After 300 sec., the potential increases slowly and eventually saturates around 600 sec., which is associated with the Cu-on-Cu deposition. This growth of the Cu layer leads to a continuous lowering of the Rs value.}

Figure 3. Linear sweep voltammograms for (a) EDTA-only (0.15 M) solution (b) Cu-EDTA solution with free EDTA [EDTA]/[Cu] = 6, for a certain timeframe during which the system was left at OCP. Conditions: $40^\circ \text{C}$, the scan direction was positive, scan rate $2 \text{ mV/sec}$. Figure 4. Cyclic voltammogram of Cu-EDTA solution without free EDTA (CR = 1). The scan was started at OCP, scan rate $2 \text{ mV/sec}$. Figure 5. Cyclic voltammogram of Cu-EDTA solution without free EDTA (CR = 1). The scan was started at OCP, scan rate $2 \text{ mV/sec}$. Figure 6, for a certain timeframe during which the system was left at OCP. Conditions: $40^\circ \text{C}$, the scan direction was positive, scan rate $2 \text{ mV/sec}$.
From both literature and the results described here, the following understanding was obtained concerning the Cu-EDTA concentration ratio. On one hand, it is important that the bath should not contain free EDTA because this can assist in a Co oxidation and corrosion process. On the other hand, however, the complexing agent can also improve the bath stability by preventing the formation of Cu precipitates (when for a Cu-EDTA mixture the EDTA concentration is lower than the Cu ion concentration, Cu(OH)₂ formation takes place). Furthermore, Shu et al. also reported that when the molecular concentrations of the Cu and EDTA are identical (CR = 1), the Cu(OH)₂ formation increases with increasing OH⁻ concentration. In addition, we found that the solution should not be too concentrated; a particle precipitation (most likely consisting of Cu₂O) is observed when the concentration of Cu-EDTA was higher than 0.5 M and omitting a stabilizer (2,2′-bipyridyl).

To obtain high quality interconnects, metal corrosion issues should be absent both in the metallization sequence as well as during CMP. Especially in case the layer is only a few nanometers thick (damascene-type of interconnects) or when there is a layer thickness non-uniformity (high aspect ratio features), a more thorough understanding is needed in order to avoid corrosion. Presently, a more detailed study is ongoing focusing on additional parameters such as temperature, free EDTA concentration, the presence of corrosion inhibitors, and the oxidation state of Co. All these parameters can be expected to play a role in the corrosion kinetics, as well as have an impact on the nucleation of any wet-chemical deposition on metal liners.

**Electroless Cu seed deposition on CVD-Co in 3 × 50 μm TSV.**—Figure 6 shows the cross-sectional TEM images of a 3 × 50 μm TSV with the Co liner before the ELD Cu process. A good contrast between the different layers is present (Co black, TiN gray, and SiO₂ white). Grains of 5–10 nm in size were observed inside the Co layer, which indicates the CVD-Co film is crystalline. The TiN layer is smooth and has a constant thickness of 12 nm over the entire depth of the TSV. The thickness of the CVD-Co layer is 45–50 nm at the top of the TSV, and decreases toward the bottom of the TSV with 30 nm in the middle and 12 nm at the bottom.

Figure 7 shows cross-sectional TEM images of a 3 × 50 μm TSV from the same wafer as Figure 6, however, after the glyoxylic acid based ELD Cu process. The ELD used same concentrations of Cu ion and EDTA (CR = 1). No voids are detected in the stack and the Cu surface is much smoother than that of the pristine CVD-Co surface (compare to Figure 6). Even though the TiN and SiO₂ are distinguishable in these images, it is difficult to identify the Cu and Co layers in the regular TEM images. Using the energy-filtered (EF) TEM, however, the Co and Cu layers can be clearly distinguished. From the Cu signal, it can be seen that the ELD Cu layer is continuous at the sidewall of the TSV. From top to bottom, there is only a 10 nm decrease in thickness of the ELD Cu layer, which demonstrates that this is an excellent seeding layer for high AR structures. Cobalt was not detected at the bottom of the structure. Nevertheless, the Cu was deposited and this means that some Co liner must have been present at these locations prior to ELD Cu. Possibly, local concentrations of bath components in high aspect ratio features are different from the bulk concentration due to diffusion limitations, which can impact local corrosion.

The stack shown in Figure 7 continued for an electrochemical Cu fill to demonstrate the potential of this Cu seeding process. Figure 8
shows cross-sectional FIB images of the TSV after ECD Cu filling. There are no voids observed inside the TSVs. However, some slit voids (suggesting layer delamination) are observed at the TSV sidewall near the top (Figure 8b). These defects can be ascribed to a vacuum break in between the TiN barrier and Co liner deposition steps (similar voids were observed in stacks of PVD-Cu/ALD-TiN with a vacuum break in between the steps). On the other hand, no slit voids were observed in control experiments with PVD-Cu/PVD-Ta stacks for which no air exposure occurred (data not shown). After the electrochemical Cu fill, the total in-field film thickness was only 600 nm. To obtain a similar Cu fill when using a PVD-Cu seed, i.e. ensuring sufficient sidewall coverage, the required Cu seed thickness was 1500 nm in the field area. Thus, the thin Cu overburden generated using a combination of our ELD Cu seeding and the TSV filling process enables a significant cost reduction for the consecutive chemical mechanical polishing step of the Cu overburden.

Conclusions
A continuous and thin seed layer was formed by glyoxylic acid based Cu electroless deposition on a Co liner in TSVs. In contrast to formaldehyde, glyoxylic acid showed anodic oxidation on Co. The electrochemical data presented in this work show that the concentration ratio of EDTA and Cu ions is important for realizing a good control of the replacement reaction between Cu and Co. When there is no free EDTA available in the electroless bath, there is no oxidation of Co by EDTA. This particular bath composition was, therefore, used to minimize a possible Co etching at the bottom of the 3 × 50 μm TSV.

The seed deposition in this high AR structure was successful over the whole depth of the TSV. The resulting 20–30 nm Cu seed layer enabled the void-free fill by electrochemical plating of Cu. The ELD Cu seeding can contribute to a significant cost reduction of the CMP process that is needed to remove the Cu overburden. This study is a proof-of-concept that a Co liner can be used in TSV metallization sequences which are extendable for filling high aspect ratio structures in future technology nodes.

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