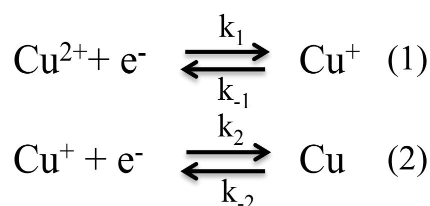
Abstract of the Dissertation

Cuprous intermediates, that include cuprous ions and complexes, are the key for copper electrodeposition. They not only accumulate at the bottom for filling up mechanism but also adsorb to improve mechanical properties of deposited copper. However, there have been only a few researches on cuprous intermediates.[12-19] The copper electrodeposition occurs with two steps, written as reactions below:



The first step is the reduction from cupric ion to cuprous ion. The second step is the reduction from cuprous ion to deposited copper. k_1, k_{-1}, k_2, and k_{-2} are the reaction constants for the forward and reverse reactions of the first and second step, respectively. According to N. Tantavichet[13], k_1 is 2 x 10^{-4} while k_2 is 130, million times larger than k_1. That means the reduction of cuprous ion is spontaneous and cuprous ion is disappeared rapidly. Beside fast reduction to copper, cuprous is also transparent and odourless. Therefore, it is really hard to measure cuprous ions produced in copper electrodeposition. The ring electrode of RRDE has been used for determination of cuprous intermediates formed during anodic polarization process. Generally, the dissolution of copper on disk electrode occurs in two steps, firstly the oxidation of Cu to Cu^+, followed by the oxidation of Cu^+ to Cu^{2+}. Because of high rotation speed, the Cu^+ ions are swept to the ring. The ring potential is kept positive to oxidize all Cu^+ ions. Then, the cuprous ions produced during dissolution process on disk are measured as the ring

current. J. R. White reported that the ring current of cathodic polarization is about 0.1 μA and that of anodic polarization is approximately 100 μA, this means the amount of cuprous intermediates at the anodic polarization is 1000 times higher than that at the cathodic polarization.[9] Therefore, K. Kondo measured the increases in the ring current at anodic polarization and suggested a bottom-up filling mechanism that involves the formation of Cu(I)thiolate complex and cuprous ion.[16,17] However, no one to date monitored the relations between additive concentration and cuprous intermediates amount for deeper investigating and controlling the copper electrodeposition. Therefore, in this research, I focused on investigating the cuprous intermediates by CVS using a RRDE to qualitatively and quantitatively control the copper electrodeposition process. Beside electrochemical measurements, mechanical characterizations of deposited copper were also conducted to evaluate the accuracy of the monitoring method.

In Chapter 2, I investigated and compared the acceleration effect of two accelerators SPS and PDSH in the presence of halide ions Cl^- and Br^- by linear sweep voltammetry stripping (LSV) using RRDE. The cuprous intermediates total amount was measured as the ring current. By comparing the amount of cuprous intermediates formed during copper dissolution on disk electrode of copper electrodeposition process, the best electrolytes for copper electrodeposition was determined. Then, TSV fillings at this optimal concentration of PDSH were conducted.

In Chapter 3 and Chapter 4, a CVS method using RRDE was used to monitor the concentration of key additives (SPS and 2M5S) in electrodeposition solution. SPS plays an important role on accelerating the

bottom-up filling, leads to void free filling.[49-62] However, SPS contains a disulfide linkage that is unstable, easily decomposed through oxidation reactions at anode or reduction reactions at cathode.[63-70] The decrease of SPS concentration in electrodeposition solution results in voids. Therefore, the monitoring of SPS concentration in electrodeposition solution is important for maintenance of void free fillings. Meanwhile, 2M5S is crucial for achieving the reduction of copper TEC.[71,72] This reduction is explained by the incorporation of 2M5S to electrodeposited copper. However, because of the incorporation, 2M5S is consumed during copper electrodeposition. This consumption is the main reason of the deterioration of low TEC electrolyte. Both SPS and 2M5S were monitored by the relationship between their concentrations and the ring current. Beside electrochemical measurements, the TSV fillings are carried out to evaluate the accuracy of monitoring method for SPS. In addition, thermal expansion of copper pipe was measured to check the efficiency of monitoring 2M5S.

Copper to copper wafer hybrid bonding is the most promising technology for 3D integration.[73-83, 86-90] The copper direct bonding process eliminates the need for solder and anisotropic conductive film. In addition, copper direct bonding allows manufacturing smaller image sensors at a higher rate of productivity with the elimination of TSV connections area. This technology helps further chip size reduction. In the hybrid bonding process, two silicon wafers are aligned and contacted. At room temperature, these aligned copper pads contain radial-shaped nanometer-sized hollows due to the dishing effect induced by CMP. To overcome the dishing effect, these wafers are annealed at high temperature for copper to expand and connect upper and lower pads. However, for hybrid bonding at low

temperature, dishing effect is still challenging. In chapter 5, I investigated the new high TEC electrodeposited copper to eliminate the dishing hollows at lower temperature than that with conventional copper using the combination of new additive A and low TEC additives. The illustration of role of each additive in high TEC electrolyte was suggested following the experiment results. Furthermore, The contact area of copper pads was estimated with new value of copper TEC. Lastly, Chapter 6 summarizes the main contributions of this dissertation.