Characterization of Low-Temperature Selective Cobalt Atomic Layer Deposition (ALD) for Chip Bonding

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Abstract— A Cu-Cu bonding approach using low temperature (200 °C) selective Co ALD is demonstrated for Cu pads that are separated by 200 nm. The bonding testbed is characterized before and after Co ALD by SEM and EDS to confirm the feasibility of the approach. AFM and XPS are used to measure the selectivity of Co ALD on Cu and SiO₂ surfaces.

Keywords—ALD Bonding, Selective Co ALD, Low Temperature, Cu-Cu Bonding, Chip Bonding

I. INTRODUCTION

Heterogeneous integration is a promising approach to continue increasing system performance as Moore's Law begins to slow. A common approach today is to disaggregate the functions of a large and complex monolithic IC into multiple smaller 'chiplets.' Each chiplet can be fabricated using optimized fabrication processes for its function thereby improving performance and energy efficiency. Moreover, the resulting smaller area of the chiplet can improve wafer yield and lowers costs [1].



Figure 1 The concept of ALD bonding

To interconnect chiplets on a single package, traditional approaches use micro-bump bonding technology. Micro-bump bonding relies on melting a tin-based solder to form the interconnections [2]. However, during bonding, the liquid solder can cause bridging of adjacent bonds at fine pitches and thus, new interconnection methods are needed to scale down I/O pitch.

Conversely, solder-free Cu-Cu bonding represents a promising path towards I/O pitch of smaller than 50 micrometers [3]. Several major Cu-Cu bonding methods have been developed and most of them are based on thermal-compression methods. However, all methods have their own drawbacks and require some level of mechanical bonding force, CMP, or high bonding temperatures. For example, the

Surface Activation Bonding (SAB) process is based on Cu pad surface cleaning using plasma to decrease the bonding temperature; however, this process requires extremely low chamber pressure [4]. The Self-assembled Monolayer (SAM) method prevents surface oxidation by coating the Cu pads with a monolayer of alkanethiol group as protection, yet the process needs large mechanical bonding force and high-temperature annealing [5]. The "Hybrid Bonding" process utilizes the surrounded oxide as mold to force the Cu bumps to expand and bond during anneal to eliminate the underfill material/process; this approach requires precise CMP down to less than few nanometers deviation [6].

We have recently proposed and demonstrated a new method, as shown in Figure 1, to bond copper pads using Atomic Layer Deposition (ALD) of selective Cobalt (Co) to successfully bond Cu pads [7]. Co ALD, which is deposited at approximately 200 °C, can bond two Cu pads without an external mechanical force to prevent chip cracking and does not require extreme CMP to planarize the Cu surface. ALD is performed by alternating two self-limiting precursors so the Co film's thickness can be controlled at the angstrom range. This exceptional controllability provides the potential to shrink the Cu I/O pitch to the 100's of nanometer scale.

II. EXPERIMENT

Shown in Figure 2, the testbed consist of a three-layered structure that contains a 200-nanometer thick SiO₂ in between a top and a bottom Cu layers. The 200-nanometer thick SiO₂ is a sacrificial layer that is removed by buffered oxide etch (BOE) to create a uniform 200 nanometer gap in between the top and bottom Cu layers prior to ALD bonding. The top Cu layer serves as an interconnect bridge between two neighboring bonding-pads (on the bottom layer) once the Co is deposited within the gap. The bottom Cu layer contains 20 μ m x 20 μ m bonding-pads on a 30 μ m pitch; each of the bonding-pads is connected with two probing-pads to enable resistance measurements. 50 μ m and 100 μ m pitch testbeds are also made.



Figure 2 (a) The bird's-eye view70fthreforAd21, 2011 EEE testbed (b) Close up view of the Co ALD bonding testbed

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The detailed fabrication steps are shown in Figure 4. Firstly, the bottom Cu layer is formed using PVD lift-off of a 150 nm thick Cu film with a 15 nm thick Cr film as an adhesion layer on Si₃N₄. Second, a 200 nm thick SiO₂ is deposited by PECVD with a 15 nm thick Ti adhesion layer. Third, the top layer of Cu, which is 1.5 μ m thick, is formed using PVD lift-off with 15 nm thick Ti layer. The fourth step is to remove the SiO₂ sacrificial layer and the Ti adhesion layers using BOE for 10 min. The reason why Cr is selected as the bottom Cu layer's adhesion layer is because Cr has a slower etch rate compared to Ti or SiO₂ in BOE. Following this step, the testbed is ready for Co ALD deposition to create bonding in between the top and bottom Cu layers.

In this work, thermal selective Co ALD, with a pre-cleaning step, is used to deposit 100 nanometers of Co on the Cu exclusively to form a bond at low temperature. The precleaning step is a 30 min anneal at 350 °C under UHV and is performed prior to Co ALD deposition to ensure all the organic residues are removed.

As for the deposition, the thermal selective Co ALD deposition utilizes *tert*-butylamine (TBA) and bis(1,4-di-tert-butyl-1,3-diazadienyl)cobalt (Co(DaD)₂) as precursors and alternates between these two precursors to reach a self-limiting reaction that deposits Co under 200 °C at 10 Torr. The full deposition cycle is Co(DAD)₂ (5.0 s)/ turbomolecular pumping (10.0 s)/ tert-butylamine (0.2 s)/ turbomolecular pumping (10.0 s). Each cycle deposits 1 Å of Co, repeating 1,000 cycles to grow 100 nanometers of Co on the top and bottom layers of Cu in order to bond the 200-nanometer gap. The Co(DaD)₂ precursor preparation, growth condition and mechanism have been extensively studied in the past [8].



Figure 4 Fabrication steps of the Co ALD bonding testbed

III. RESULT & DISCUSSION

A. -Cross-section Before and After Co ALD Bonding

FIB-SEM is used to create a cross-sectional image at the bonding pads before and after ALD deposition. Before ALD deposition, Figure 5 (a) shows a 200-nanometer gap separating the top and bottom Cu layers. The top Cu layer is $1.5 \mu m$ thick and serves as the bridge for the bottom 150



Figure 5 The cross-sectional view at the bonding-pads by FIB-SEM



Figure 3 The SEM and EDS characteristics of the bottom Cu surface before ALD bonding

nanometers thick Cu pads. After ALD deposition, Figure 5 (b) shows the successful gap filling by Co with 1,000 cycles of deposition. Further characterization will be discussed later in the paper. From the previous study, electrical measurements were also conducted to prove the connectivity by comparing the resistance before and after Co ALD bonding [7].

B. -The Surfaces Before & After ALD Deposition

Before Co ALD deposition, the testbed is placed in a BOE etch to remove the SiO_2 sacrificial layer and Ti adhesion layer. To confirm the SiO_2 sacrificial layer and Ti adhesion layer are properly removed before Co ALD deposition, Figure 3 shows SEM and EDS measurement of the bottom Cu bonding-pads after 10 min of BOE etch. The bottom Cu layer has a thin Cr adhesion layer atop the Si_3N_4 substrate, contributing to the Cr signal in the EDS. The Si_3N_4 substrate's nitrogen signal is not detected due to the 150 nm thick Cu bonding-pads, which can significantly attenuate the signal intensity.

Figure 6 shows the SEM and EDS measurements of the peeled top Cu layer after 10 min of BOE etch to confirm that the top Cu layers are 'clean' without Ti. Due to the peeling force, the top Cu layer is not flat under SEM. The dark center areas in Figure 6 (a) and (b) are the Ti adhesion layer that was not etched inside the gap, as also shown by the EDS measurement in Figure 6 (a). From this region, we estimate that approximately 40 µm of Ti is laterally etched in a 200 nm thick gap. The remainder of the light-colored region in Figure 6 (b) has been shown experimentally to be Cu area without Ti. The surfaces of the top and bottom Cu layers after 1,000 cycles of Co ALD deposition are shown in Figure 7. Figure 7 (a) is the bottom Cu bonding pads, and Figure 7 (b) is the top Cu layer that was peeled off after Co ALD Bonding. The EDS measurement confirms that Co is deposited on both the top and bottom Cu surfaces. These results are consistent with the finding in Figure 5 that show Co has filled and bonded the gap between the top and bottom Cu layers. It is worth noting that the width of the top Cu layer in Figure 7 (b) is less than 40 μ m, and thus, the Ti film was removed by BOE which is verified with EDS.



2 Figure 6 The SEM and EDS characteristation of the top of the 1.00 ©2021 IEEE layers before ALD bonding

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Figure 7 SEM and EDS of (a) Bottom Cu bondingpads after 1,000 cycles of Co ALD (b) Top Cu layer

C. -Selectivity Study



Figure 8 XPS of Cu and SiO2 during different cycles

To understand selectivity for 350 °C pre-cleaning process, Cu and SiO₂ film are measured by XPS and AFM under different cycles of $Co(DaD)_2$ + TBA deposition. The Cu is prepared by PVD and the SiO₂ is fabricated by LPCVD with 0.5 % HFcleaning. The XPS study of Cu and SiO₂ is shown in Figure 8. Before Co ALD deposition, the pristine Cu surface has 94% of Cu signal after the 350 °C anneal for 30 min at UHV pressure. The Cu signal decreases to 5.5% and the Co signal increases to 56% just after 50 cycles, meaning the Cu surface is almost buried by Co deposition. As for 250 cycles of Co deposition, the Cu surface's Cu signal further decreases to 1.3% and the Co signal increases to 59%. The 0.5 % HF-cleaned SiO₂, on the other hand, shows almost no Co signal throughout the precleaning up to 250 cycles. The AFM study of Cu and SiO₂ is shown in Figure 9. The surface roughness of Cu and SiO₂ after 250 cycles of Co ALD indicates a large selectivity difference. The Cu, after deposited with Co, has a root-mean-square roughness of 1.4 nanometers with some 3~4 nanometer high of Co nuclei. As for the SiO₂ surface, the surface root-mean-HF-cleaned SiO Cu



Figure 9 AFM measurement of the Cu and SiO₂ surfaces after 250 cycles of Co ALD deposition

square roughness is only 0.32 nanometers without noticeable Co nuclei in most areas. These results demonstrate selectivity of Co between a metal and a dielectric material, which is consistent with the previous studies.

IV. CONCLUSION

Low temperature (200 °C) selective Co ALD is shown as a potential Cu-Cu bonding approach to connect Cu pads separated by 200 nm gap and 30 μ m pitch. Cross-sectional images of the Cu layers after ALD bonding show Co infilling within the gap to create the interconnections. SEM and EDS analysis were also used to confirm the Co deposition. Lastly, Co ALD selectivity studies on SiO₂ and Cu with different deposition cycles show excellent selectivity under 350 °C precleaning.

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