Optimization of the Copper Microstructure to Improve Copper-to-Copper Direct Bonding

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Abstract
Advanced packaging solutions and heterogeneous integration are key technologies to enable devices with improved operating characteristics, including higher performance, increasing power efficiency, and decreasing form factor. Packages with high interconnect densities are required to efficiently combine, e.g., processing and memory units but impose restrictions to the pitch of the interconnects. Conventional technologies, including wire bonds and flip chip bonds are limited to larger pitches and, therefore, not suitable to meet the requirements of upcoming packaging technologies with respect to interconnect densities. Direct copper-to-copper interconnects are supposed to allow such small pitches of 10 µm or even below. However, formation of such bonds usually requires high temperatures and pressures. Temperature-sensitive devices like DRAM components restrict the maximum temperature that can be applied to the package. Thus, copper material is required, which allows bond formation at relatively low temperatures. In this context, hybrid bonding processes were discussed that involve initial bond formation via the usually oxide-based dielectric at room temperature followed by copper-to-copper bonding at elevated temperatures. The copper material is usually prepared by electrolytic deposition and the properties of the respective deposits may be modified by properly designed organic additives as well as process parameters. Strong bond formation of the copper should be obtained upon grain growth over the interface of the two deposits, which are brought into contact during the bonding step. In order to facilitate such growth at relatively low temperatures, suitable microstructures need to be prepared. Ideally, morphologies should be chosen in a way that they can be maintained throughout all process steps after the electrolytic deposition but, at the same time, allow grain growth over the interface during copper-to-copper bonding. Various strategies to enable improved seamless grain growth but maintain a metastable microstructure throughout the preceding process steps and the corresponding unique copper microstructures will be compared. In this context, different electrolytic copper deposition processes, the resulting microstructures, as well as their respective advantages and challenges with regards to copper-to-copper bond formation will be discussed.

Key words
copper-copper direct bonding, copper electrodeposition, hybrid bonding, microstructure

I. Introduction
Advanced packaging approaches that allow high interconnect densities for upcoming applications rely on heterogeneous integration and 3D connections of components within the packages. [1] Copper constitutes the main interconnect material for the individual components as well as for their packaging. [1], [2] Connection of the components via different bonding technologies is required to fabricate the assemblies and conventional techniques rely on wire bonds and flip chip applications. [1], [3] The latter involve copper bumps and pillars in combination with solder material based on either tin or tin-silver alloys. [1], [4], [5], [6], [7] The corresponding layers are usually produced by electrodeposition. However, common processes usually suffer from relatively large non-uniformities in the range of several micrometers, especially with regards to coplanarity, although the solder material allows for compensation of the differences to some extent during reflow and bond formation. Increase of the interconnect density involves shrinking pitch, i.e., the distances between the connections.
Wire bonding and flip chip technologies are not suitable for fine pitch applications due to their respective spatial requirements. Wire bonds usually require spaces in the range of 50 µm, while flip chip applications are predicted to be limited to pitches of more than 10 µm. The solder material could be squeezed out from the structures during bonding and, thereby, create electrical shorts. [8] Direct formation of copper-to-copper interconnects allows to overcome these issues by omitting conventional solder bumps of flip chip technologies and to decrease the pitch to values distinctly below 10 µm. [9]

Direct copper-to-copper contacts were initially established by thermocompression bonding. [10] However, this technology required significant thermal budgets and elevated temperatures, which may lead to degradation of sensitive dies that are used, e.g., in DRAM packages. [11], [12] Further issues included warpage and package reliability. In addition, challenges may arise from extensive oxide formation on the copper surface at such elevated temperatures. [13], [14] In order to overcome issues of temperature-sensitive devices, a low-temperature bonding technology was required. In this context, hybrid bonding is considered as promising alternative. [12], [14], [15] This technology was successfully employed for high volume manufacturing of image sensor packages and for stacking memory with sensor and logic components. [16], [17], [18] The hybrid bonding process includes copper electrodeposition, chemical-mechanical polishing (CMP), and oxide-to-oxide bonding at room temperature followed by formation of the copper-to-copper interconnects at moderately increased temperatures. Initial oxide-to-oxide bond formation allows to adhere the wafers or dies that are supposed to be connected and occurs spontaneously at room temperature. Further chemical bond strengthening of the oxide takes place during an annealing step that is required for formation of the copper-to-copper bond. The corresponding temperatures should be limited to approximately 200 °C to be compatible with sensitive devices. Significant efforts were required to develop suitable process steps for hybrid bonding, including the optimization of cleaning and preparation of the surface for bonding, the CMP process, pitch scaling, as well as alignment for wafer-to-wafer as well as die-to-wafer applications. [12], [14], [15] In particular, the CMP process was identified as key step to allow distinct advantages of hybrid bonding over thermocompression bonding. [12], [15] Furthermore, recent studies emphasized the necessity to optimize the copper electrodeposition process for hybrid bonding. Previous work suggested improved bonding upon interdiffusion of copper atoms and growth of grains over the bond interface. [10], [14], [15], [19], [20] However, such growth was associated with extensive annealing at high temperatures for long times and at elevated pressures. Recently, the influence of copper deposits with different microstructures, including coarse-grained, nano-twinned, and fine-grained morphologies were compared with regards to the required thermal budget in hybrid bonding. [21] Resistivity evolution upon application of different thermal budgets suggested best bond formation for the fine-grained structure. Electron backscatter diffraction (EBSD) revealed some growth of grains through the bond interface at temperatures of 250 °C. However, due to co-deposited impurities, bonding was accompanied by accumulation of micro-voids. In our previous work, a strategy to optimize bond formation with regards to grain growth through the interface at temperatures of 200 °C and even below in combination with high purity copper to prevent void formation was proposed. [7] A fine-grained microstructure with high deposit purity and via filling performance could be obtained by employing properly designed organic additives and process parameters. This structure was rendered metastable and growth of grains over an interface at relatively low temperatures emphasized the potential of this approach for copper-to-copper direct bonding. The fine-grained deposit that allowed copper bond formation by grain growth could be maintained for approximately 12 h in this work. While such times might in some circumstances be suitable for wafer-to-wafer bonding, die-to-wafer bonding processes require significantly longer times.

In this work, we compare different copper morphologies with regards to microstructure evolution, specific resistance, and potential for further grain growth through the copper-to-copper interface upon bond formation. The results were expected to reveal the potential of metastable copper. In order to be able to apply this type of copper to typical integration process flows, additional strategies to maintain the metastable microstructure for longer times are presented. Comparison of wafer-to-wafer bonding results from stable and metastable microstructures was supposed to demonstrate improved bond formation.

II. Results and Discussion

A. Experimental Section

Electrodeposition of copper layers with different microstructures was performed on an Autolab potentiostat/galvanostat (Metrohm, PGSTAT 302N) in combination with a rotating disc electrode (RDE) setup using a coupon holder as working electrode. Coupon-scale substrates were cut from blanket 300 mm and mounted to the coupon holder. A soluble copper electrode served as counter electrode. Prior to the electrolytic process, the coupons were treated with diluted sulfuric acid (10%) for 20 s. All copper electrodeposition experiments were performed at 298 K. An aqueous, additive-free base electrolyte, consisting of cupric sulfate, sulfuric acid, and chloride was used as base
electrolyte. Fine-grained, nano-twinned, coarse-grained, and metastable copper deposits were prepared by electrodeposition from the base electrolyte in the presence of commercial and experimental additives of the Spherolyte Cu series (Atotech).

Preparation of structured 300 mm wafers, electrodeposition with suitable process parameters and additives of the Spherolyte Cu series (Atotech), as well as wafer-to-wafer bonding was performed at Fraunhofer Institute for Reliability and Microintegration (Fraunhofer IZM-ASSID). Bonding from the stable microstructure was achieved by annealing at 200 °C for 1 h after copper electrodeposition prior to CMP. Bond formation from the metastable microstructure was performed by restricting the time between electrolytic deposition and copper-to-copper bond formation to ≤ 20 h.

B. Optimization of the Copper Microstructure

Various copper deposits were prepared by electrodeposition in the presence of a series of organic additives. The corresponding microstructures are depicted in Figure 1 and included fine-grained, nano-twinned, coarse-grained, and metastable structures. The fine-grained copper exhibited small grains, presumably due to inhibited further growth as a consequence of decreased deposit purity (Figure 1a). Impurities originated from co-deposition of organic additives, [22], [23] and resulted in significantly increased temperatures that were required for formation of larger grains. [7] Although such fine-grained deposits were proposed for improved bond formation by growth of grains through the interface, [21] the necessity for elevated temperatures beyond the requirements of sensitive devices and void formation caused by accumulation of co-deposited impurities are detrimental for hybrid bonding. Nano-twinned copper was proposed for copper-to-copper bonding and showed columnar grains with horizontally oriented twins at distances in the nanometer regime (Figure 1b). [24], [25] Coarse-grained copper with large, randomly oriented grains was obtained by preparation of deposits of high purity in the presence of suitable organic additives (Figure 1c). [23] Significantly improved purity by negligible co-deposition of the additives allowed preparation of copper microstructures that required very low temperatures and short times to grow large grains, whose size was in the order of the deposit thickness. [7], [23] Once the final grain size was obtained, the structure was relatively stable and exhibited minor further recrystallization. A metastable microstructure with very small grains and high deposit purity could be achieved by a proper combination of organic additives and process conditions (Figure 1d). [7] This type of copper was supposed to allow grain growth through the bond interface and, due to its purity, avoid impurity-related issues such as high temperatures for grain growth and void formation. Conductivity measurements were performed to reveal the suitability of the different microstructures for copper-to-copper direct bonding applications. Table I shows the specific electrical resistance values for the different microstructures depicted in Figure 1. Noteworthy, the values for fine-grained, nano-twinned, and stable, coarse-grained structures were obtained after annealing for 1 h at 200 °C. These conditions were supposed to mimic copper-to-copper bond formation. The value for the metastable copper was determined directly after deposition, since this morphology was optimized for a transition to a microstructure, which would resemble that of the stable, coarse-grained example after application of this thermal budget. The lowest specific resistance was obtained with the coarse-grained microstructure, which may be related to large grains and high deposit purity. Fine-grained copper showed increased specific resistance in comparison to the coarse-grained structure, presumably due to increased grain boundaries and co-deposition of impurities. The specific resistance of nano-twinned copper was significantly higher than that of coarse-grained deposits, which may be related to the high-angle grain boundaries of the columnar structures. Comparison to the fine- and coarse-grained structures under the same annealing conditions was in good agreement with previously reported high temperatures that were required for grain growth of impure deposits. The highest specific resistance was obtained for the metastable structure, which may be related to very small grains and the resulting large number of grain boundaries.

![Figure 1. FIB/SEM cross-sections of fine-grained (a), nano-twinned (b), coarse-grained (c), and metastable (d) copper microstructures.](image)

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<tr>
<th>Copper microstructure</th>
<th>$\rho$ [µΩ cm]</th>
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<tbody>
<tr>
<td>Fine-grained</td>
<td>1.95 $^a$</td>
</tr>
<tr>
<td>Nano-twinned</td>
<td>1.96 $^a$</td>
</tr>
<tr>
<td>Coarse-grained</td>
<td>1.80 $^a$</td>
</tr>
<tr>
<td>Metastable</td>
<td>2.10 $^b$</td>
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$^a$ Determined after annealing for 1 h at 200 °C.  
$^b$ Determined after deposition.

In a next step, the variation of the specific resistance as a
function of time was investigated to obtain insights into the microstructure evolution after deposition (Figure 2). Changes of the resistance may be correlated to time-dependent variation of the respective microstructures. In agreement with small grains and high impurities, the fine-grained deposit showed the highest initial specific resistance value, which decreased after 120 h to the value that was found after annealing. Nano-twinned copper did not exhibit variation of the resistance within the error of the experiment, indicating no changes of the microstructure. All values were close that after annealing. The stability of the microstructure and absence of self-annealing may potentially be beneficial for typical copper-to-copper direct bonding process flows. The metastable deposits showed high initial specific resistance, which decreased after 120 h to the value for coarse-grained copper after annealing. In agreement with previous studies of the microstructure evolution over time, [7] no significant modification of the resistance was observed after 30 h. Changes of the microstructure after relatively long times at room temperature in combination with significant grain growth at low temperatures indicated the potential of metastable copper for copper-to-copper direct bonding.

The different steps of the overall hybrid bonding process prior to formation of the copper-to-copper bond are usually performed at either room temperature, e.g., the copper electrodeposition process itself and oxide-to-oxide bond formation, or below, e.g., the CMP process. Therefore, the metastable copper structure that allows for grain growth through the interface was previously rendered metastable at 25 °C by suitable process conditions. [7] Comparison of different process parameters 1 and 2 revealed prolonged times for recrystallization from less than 9 h for transition to the stable, coarse-grained structure to no significant grain growth after 12 h (Figure 3a). Further optimization resulted in parameter set 3 that allowed to maintain the microstructure even longer for ca. 20 h at room temperature. Such timescale might potentially be sufficient for wafer-to-wafer bonding. However, die-to-wafer bonding requires process times in the order of two weeks. Proper post-treatment with otherwise identical process parameters eventually provided sufficiently persistent metastable microstructures (Figure 3b). No noticeable grain growth could be detected over a period of two weeks. After a period of three weeks, advanced transition to the stable microstructure was ultimately observed.

C. Copper-to-Copper Bonding

Based on the specific resistance values as well as deposit purity, stable and metastable copper deposits were compared with regard to copper-to-copper direct bonding. Formation of the bonded samples was performed by means of wafer-to-wafer bonding, using a hybrid bonding process.
flow. Representative scanning electron microscopy (SEM) images of cross-sections of the bonded wafers prepared by focused ion beam (FIB) are depicted in Figure 4. Copper-to-copper bond formation was achieved at 200 °C applied for 1 h. Bonding from the stable microstructure resulted in contact of the two copper structures. However, no growth of grains through the interface was observed (Figure 4a). Additional annealing was applied to the bonded structures to mimic the thermal budget during build-up of a package based on four copper-to-copper direct bond formations and a flip chip reflow (3 x 1 h 200°C, reflow with 260 °C peak temperature). No changes to the bonding result from the stable microstructure could be observed upon application of the additional thermal budget (Figure 4b). In contrast, areas that indicated partial growth of grains over the bond interface were detected, both after bonding and after the thermal budget that was supposed to mimic a typical package formation (Figure 4c, d). These results strongly supported our previous findings and the potential of the metastable microstructure for copper-to-copper direct bonding.

In addition, the colors between the two bonded copper deposits, which represent the respective grain orientations, were distinctly different, indicating that the orientations were very different from each other. Partial growth of grains through the interface was observed upon bonding from the metastable microstructure (Figure 5c). The colors in the remaining areas were much closer to each other in comparison to the result from the stable microstructure, which implied that the grain orientations generally assimilated to a large extent. The additional thermal budget led to largely matched grain orientations (Figure 5d), i.e., that the assimilation after bond formation from the metastable structure progressed even further under these conditions.

Further insights into the growth of grains over the bond interface were obtained by electron backscatter diffraction (EBSD). Figure 5 shows representative grain orientations in normal direction parallel to the direction of the copper deposition. In agreement with the FIB/SEM images, no growth of grains through the bond interface was observed after bonding from the stable microstructure and after thermal simulation of the package formation (Figure 5a, b).

III. Conclusion
Copper-to-copper direct bonding at low temperatures was identified as the most promising technology for high performance packages and allows formation of interconnects with very small pitches. Low temperatures, especially for the copper-to-copper bond formation are required for the assembly of sensitive devices like, e.g., DRAM. Copper is usually prepared by electrodeposition and the corresponding processes need to be optimized to cope with these challenges and allow proper bond formation. In this context, different copper microstructures were compared with regards to their respective specific resistance and grain structure evolution. Fine-grained structures showed relatively large resistance values and annealing temperatures, presumably due to co-deposition of impurities and, thus, appeared not to be suitable. Accumulation of such impurities was found to eventually result in micro-voids at the bond interface. [21] Nano-twinned copper showed good stability of the
microstructure, which would be compatible to typical hybrid bonding processes but relatively large specific resistance values. Copper-to-copper bond formation at low temperatures needs to be investigated for this morphology in the future but no noticeable changes of the specific resistance may indicate that relatively high temperatures are required. Coarse-grained copper provided low specific resistance but did not allow proper bond formation during wafer-to-wafer bonding. It could be shown earlier that metastable copper allowed filling of recessed features and grain growth over an interface at low temperatures. [7] Although the specific resistance was initially higher, the values were eventually similar to those of the highly conductive, coarse-grained structure. Excellent bond formation during wafer-to-wafer bonding by assimilation of the grain orientations through the bond interface could be proven.

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References


