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Effect of chain length on low temperature gold-gold bonding by self-assembled monolayers

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The tensile strength of thermocompression gold joints formed with prior surface coatings of alkanethiol self-assembled monolayers (SAMs) depends on the chain length (n) of the SAM. Enhancement of bond strength is most significant at $n=6$ while no improvement can be achieved using octadecanethiol ($n=18$). These contrasting behaviors can be interpreted as a consequence of two dominant roles of alkanethiols that govern the bonding phenomenon, namely, the passivation of gold surfaces and the ease of mechanical and/or thermal displacement. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2906905]

Three-dimensional (3D) integration is a wafer process technology that can potentially extend the power and reach of microelectronic integration. In this technology, multiple different active layers are vertically stacked by bonding metal microbumps, such as gold, copper, or directly solder, that serve as interconnects between the layers, hence, reducing the total chip area, signal delays, and power consumption. Nevertheless, a number of challenges exist with this implementation. For instance, the integration of disparate technologies, which comprises of dissimilar materials, induces thermal stresses and places constraints on the thermal budget. Thus, lowering the bonding temperature of the bonding process between such thinned layers could be a key factor of success for this integration scheme.

Today, metallurgical interconnects such as gold or copper formed by thermocompression require relatively high bonding temperature, on the order of 300–400 °C for copper-copper bonding and at least 180 °C for gold.[1–4] While temperature requirements can somewhat be traded off with bonding pressure and time such a trade-off does not alleviate the process constraints due to the fragile nature of the 3D chip stacks. Hence lower temperatures for bonding remain highly desirable.

Gold thermocompression bonding has always been considered as an excellent interconnection method because of gold surface inertness to oxidation as compared to copper. However a gold surface is still very sensitive to ambient contamination, such as carbon and oxygen forming strong chemisorbed bonds with the metal surface.[5–7] As a result significant amount of temperature and/or pressure is needed for bond formation between two gold surfaces.[8] Our previous report had shown that by coating a gold surface with a self-assembled monolayer (SAM) (C_nH_{2n+1}SH), lowered bonding temperature can be achieved.[9] It has been proven that surface passivation by this organic monolayer plays an essential role in enhancing the bonding process. This current investigation evaluates the influence of different SAM chain lengths on the bondability between gold surfaces. We found that bond strength improvement is most significant with shorter chains ($n=6$ as compared to $n=12$). SAMs with longer chain lengths ($n=18$) lead to joint strengths slightly lower than those formed with uncoated gold for all investigated bonding temperatures. The reason for this behavior, to be discussed in this letter helps clarify how SAMs function as a moderation layer in thermocompression bonding of noble metal surfaces.

The bonding samples were fabricated by electroplating gold bumps at heights of 24–26 μm on silicon wafer before dicing to yield individual bonding chips. Substrates were prepared by sputtering 50 nm Ti, followed by 100 nm TiW, and finally 100 nm Au on 0.65 mm Si wafer. The bonding chips were then immersed into 1 mM ethanolic solution of 1-hexanethiol (C_6), 1-dodecanethiol (C_{12}), and 1-octadecanethiol (C_{18}), respectively. Kept over 24 h in a N_2-purged glovebox, a relatively good quality layer of ordered and densely packed organic molecules self-assembled onto the gold surfaces. These freshly deposited samples were then bonded in ambient at temperatures of 40, 50, 65, and 80 °C under a constant bonding pressure of 487 MPa based on initial bump area for 20 s. Uncoated gold surfaces underwent 10 min of UV/ozone cleaning before bonding. It is necessary to note that the bonder takes some time to heat and cool to the set temperature, respectively. Finally, the bonded samples were subjected to a tensile pull test using a dynamic mechanical analyzer.

Figure 1 displays the tensile strength obtained from all three types of SAM-coated samples as compared to uncoated gold joints as a function of bonding temperature. In previous results, we had shown that bond strength increases with bonding temperature[4] and our present results confirm that trend. It is apparent that among all the samples, C_6-coated gold joints exhibit the highest joint strength at all temperatures, achieving usable bond strength of about 49 MPa at a temperature as low as 40 °C. Our previous report demonstrated that C_{12} improves bonding by lowering bonding temperature.[9] Using this as a reference, C_6 even showed a greater bond improvement. In contrast, it is evident that over this range of bonding temperatures, C_{18}-coated gold joints are much weaker, even when, compared to bare gold. We attributed such observation to three aspects of bonding: surface passivation, thermal activation, and mechanical deformation.

As discussed in our previous report,[9] surface passivation is a critical factor in maintaining a clean surface prior to

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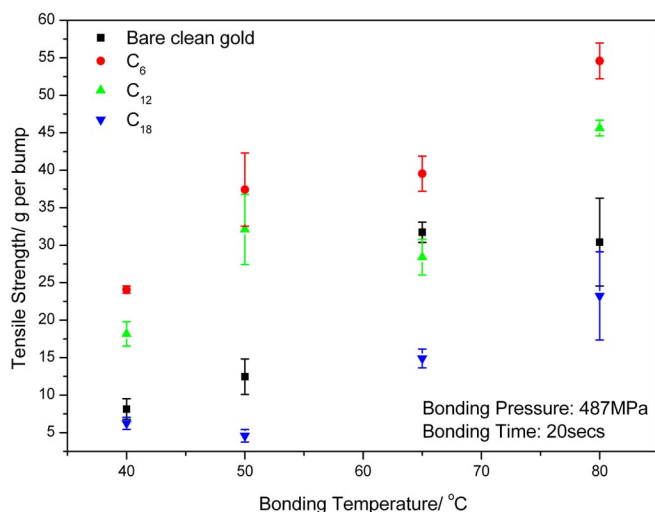
FIG. 1. (Color online) A plot of tensile strength of SAM-coated samples (C$_6$, C$_{12}$, and C$_{18}$) as compared to uncoated gold as a function of bonding temperature applied.

FIG. 2. Comparison of XPS peak area ratios of (a) O 1s and (b) C 1s at different chain lengths.

bonding. Upon exposure to the ambient, gold surfaces experience almost instantaneous contamination. To evaluate the total amount of C and O present on both coated and uncoated gold surfaces, x-ray photoelectron spectroscopy (XPS) was utilized. All XPS data were acquired using a VG ESCALAB 220i-XL instrument that is equipped with a monochromatic Al $K\alpha$ radiation (1486.7 eV photons 10^{-10} mbar background pressure), a concentric hemispherical analyzer, and a magnetic immersion lens. Since SAMs of thiolates were found to be susceptible to x-ray induced damage, where dialkyl sulfides or disulfides could form within the layer,[10,11] short scan time of the coatings was employed to avoid such effects. High resolution spectra of C 1s and O 1s for elemental quantification were recorded with pass energy of 20 eV at 0.1 eV step width. As a reference, the Au 4f peak is used for computing the peak area ratios of all elements for all samples. We observed an absence of oxygen in all SAM-coated gold samples even though the freshly coated samples were inevitably exposed in ambient for a few minutes just before loading, as shown in Fig. 2. Carbon content was also detected on cleaned gold surface despite cautious effort to minimize ambient contamination prior to chamber loading. The higher carbon content was apparent as the monolayer chain gets longer. One important point to note is that the carbon content in C$_6$ that was deposited "intentionally" on the gold surface is less than the adventitious contamination on the uncoated Au, suggesting that the ambient contaminant layer has been replaced by a milder or thinner barrier. In addition, we found that this delicate monolayer is capable of preventing further contamination during the short time span of exposure just before bonding. A smaller amount of surface contamination leads to greater ease of removal, thus, metallic bonding between the two clean surfaces can be more readily achieved.[8]

Octadecanethiol (C$_{18}$), having a longer chain length, is known to be more corrosion resistant and air stable and is therefore expected to be a stronger passivation layer.[10,12] If surface passivation is the sole factor responsible for bonding enhancement, then SAMs with longer chain lengths should be more effective than shorter SAMs. However, its poor behavior in the current bonding study clearly indicates that surface passivation is not the only determining factor influencing the effectiveness of SAM-enhanced bonding. Here,
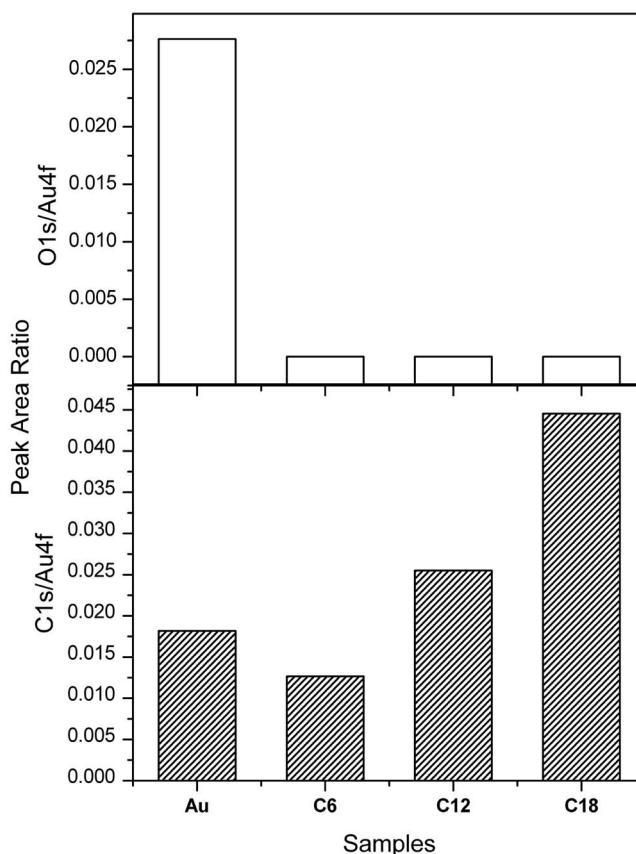
we postulate that the ease of displacement of SAMs should play an important role as well. In our experimental context, this displacement could come from the combined means of thermal desorption and mechanical deformation. During the bonding process, both the chip and substrate were heated before the two surfaces were brought into contact. Alkanethiols on gold thermally desorb in a wide temperature range, from 117 to 227 °C.[12,13] In the lower temperature range (40–80 °C) used in this work, complete thermal desorption of SAMs is not expected, thus, the displacement of SAMs by mechanical deformation becomes more important. Despite the fact that SAMs were not thermally completely displaced, heating does disrupt the orderliness of the layer and introduces defects that, can be associated with mechanical instability within the structure. This could render the monolayer more susceptible to mechanical displacement during bonding. Longer chain SAMs, such as C$_{18}$, are known for their higher thermal stability as a result of denser molecular arrangement, less gauche defects, and stronger interchain molecular forces.[14] Thus, the poor bonding results of C$_{18}$ can be interpreted as a failure of SAM displacement because of the structurally stronger arrangement of longer chain SAMs.

Then, we evaluated the ease of mechanical displacement of SAMs with different chain lengths in elucidating its role in bonding. In thermocompression bonding, the normal load applied is commonly considered to induce a shear displacement at the bonding interface, thus, deforming surface asperities and barrier layers to ensure intimate contact between the two surfaces. The bonding results imply that C$_6$-coated gold samples have the least shear resistance, resulting in the greatest ease of displacement from the gold surfaces during bonding. To investigate SAM removal by mechanical action,
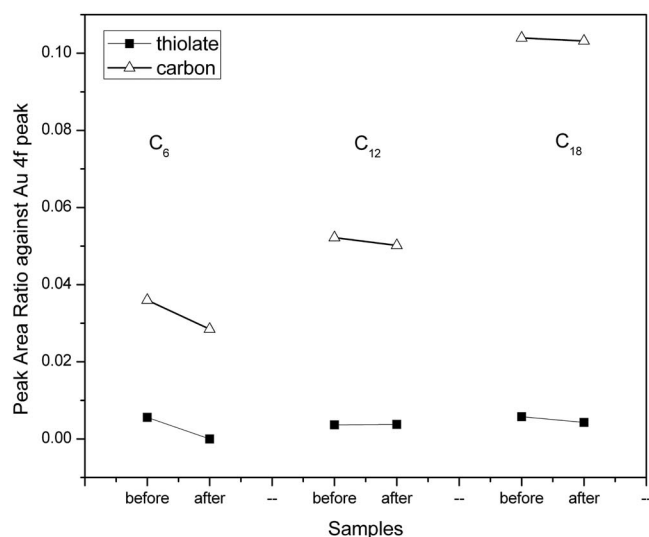
FIG. 3. Comparison of thiolate and carbon species on all SAMs before and after deformation.

the loading action during actual bonding process was simulated by pressing a SAM-coated gold surface onto a gold substrate at a sufficiently low pressure ($\sim$72.6 MPa) to avoid bonding and at room temperature (23 °C) to eliminate the thermal contribution. The reason why nonbonding conditions are used is that the loaded surfaces can be easily subjected to surface analysis.

The extent of mechanical degradation on the alkyl chains of different chain lengths was examined by measuring the combined area of the thiolate before and after deformation. The loss of thiolate can be taken as a qualitative indicator of SAM coverage on gold since the thiol group is known to strongly attach to gold. Peak area ratios of thiolate and carbon with respect to Au 4f core peak defined from the raw core spectra at binding energies (BEs) of 161.9 $\pm$ 0.1, 284.8, and 83.8 eV, respectively, were utilized to eliminate effects from sample variations. Figure 3 shows the amount of thiolate and carbon left on the gold surface prior to and after deformation for three different SAMs. Upon deformation, the greatest loss of thiolate and carbon occurs in C_6. The surface coverage after nonbonded loading is higher for C_{18} layer, suggesting that the more structurally robust the C_{18} layer is, the more it is capable of withstanding the mechanical loading. The disappearance of thiolate species implies the removal of S–Au bond, thus, freeing available pristine Au—Au bonding sites, which again support our bonding results. The lack of atomic sulfur (at BE=161 eV) (Ref. 15) after deformation also indicates that C–S cleavage did not occur, further supporting our deduction that fresh gold atoms will be available for bonding between two gold surfaces. Our findings are consistent with extensive studies in the tribological properties of alkanethiols with various chain lengths for

boundary lubricant applications.[16,17] For longer chain alkanethiols, where $n > 15$, strong Van der Waals forces of attraction between the neighboring alkyl chains allows the layer to disperse the effectively normal forces, exhibiting low friction and high wear resistance. In contrast, the shorter chain monolayers studied here ($n=2-7$) could not retain molecular order during shear, and thus can be efficiently worn away.[17]

In summary, we have demonstrated enhancement in low temperature gold-gold thermocompression bonding for both C_6- and C_{12}-coated gold surfaces. The ability of SAMs in aiding low temperature gold bonding decreases as its chain length gets longer. At $n=18$ no strength improvement is observed while at $n=6$ highest joint strength is obtained. We deduce that the consideration behind the applicability of SAMs at different chain length for bonding application depends on three primary actions at the bonding interface: (1) surface passivation to alleviate surface contamination; (2) thermal activation to "weaken" or desorb the monolayer through structural disorientation; and (3) mechanical displacement to expose virgin gold surfaces for bonding to take place.

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