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Self-assembled monolayers for reduced temperature direct metal thermocompression bonding

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A reduction in the bonding temperature required for direct gold-gold (Au–Au) thermocompression bonding is observed by coating a monolayer of dodecanethiol on gold surfaces prior to bonding. The results show that Au–Au bonded joints of 26.9 g per bump strength can be achieved at a temperature as low as 160 °C. The temperature drop becomes more apparent when both coated and blank gold samples are exposed in air over some time before bonding. The authors propose that self-assembled monolayers passivate metal surface by obviating the adsorption of surface contaminants, in particular, carbon and oxygen but get desorbed just before bonding takes place. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2768869]

In recent years, studies on three-dimensional (3D) integration have been actively pursued to meet the growing demand for increasing functionality within a single integrated chip (IC). 3D ICs facilitate dramatic reduction in wiring length by stacking multiple device layers through direct metal interconnects which are conventionally accomplished by thermocompression bonding. Since device wafers are typically thinned and hence fragile prior to bonding, it is desirable to operate at low bonding temperature and pressure. Consequently, it is essential to explore alternative approaches to alleviate temperature and/or pressure needed to form the bonds, thus enabling higher densification in 3D ICs.

Metallic microbumps of gold, copper, and eutectic solder were often favored for 3D IC applications due to the strong metallurgical bonds formed as well as their excellent electrical and thermal properties. It had been demonstrated that thermocompression Cu/Cu direct bonding[1] using a thin layer of tin (Sn) capped onto Cu bumps were formed at 240–450 °C using a bonding force of 49 N for 60 s, while for gold microjoints, bonding temperature at 350 °C was used.[2] A recent study has also shown that bonding between gold metal posts on oxide-covered silicon surfaces is possible at room temperature with no external pressure for over 60 h.[3] In this study, we demonstrate low temperature thermocompression bonding between electroplated gold bumps and gold substrate by using a monolayer of self-assembled organic molecules (SAMs) and attempt to evaluate the role of SAMs on bonding applications.

Electroplated gold bumps at bump heights of 26–29 μm were fabricated using noncyanide based gold electrolyte. The thickness of the gold substrate consisted of sputtered layers on 0.65 mm Si wafer in the following sequence: Ti (50 nm), TiW (100 nm), and 200 nm Au. To remove any hydrocarbon contaminants on the surfaces prior to SAM deposition, the gold bumps and substrates were treated with UV/ozone cleaning for 10 min, followed by sonication in absolute ethanol for about 20 min before immersing into 2 mM ethanolic solution. Kept over 24 h in a N_2-purged glove box, a layer of dodecanethiol [$CH_3(CH_2)_{11}SH$, DDT] was deposited on the gold surfaces at room temperature. The spontaneous assembly of the molecules is known to form a densely packed and highly oriented structure on the exposed gold surfaces.[4] These freshly deposited samples were then bonded in ambient at 140, 160, and 200 °C (tool temperature) under a constant bonding load of 538 g per bump for 20 s. Several minutes were necessary for the bonder to heat and cool to the set temperature. No additional cleaning steps besides solvent rinsing were employed for the blank gold samples. Similar bonding parameters were then used to bond the samples, after which the bonded samples were subjected to a tensile pull test using a dynamic mechanical analyzer.

In our experiments, we have demonstrated enhanced bond strength for the gold joints coated with dodecanethiol DDT, (C_{12}) prior to bonding. Figure 1 compares the tensile strength of both types of bonded samples as a function of

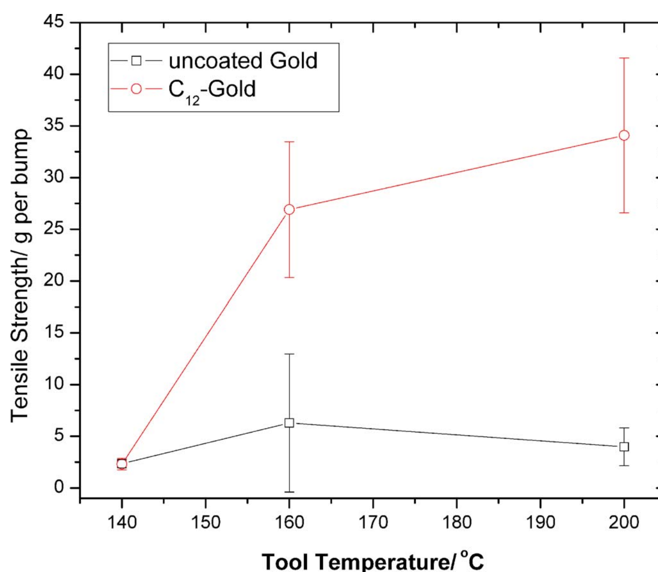

FIG. 1. (Color online) Plot of tensile strength of gold samples with and without DDT as a function of bonding temperature applied.

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tool temperature. Bond strength increases with bonding temperature, as expected. All capped joints are stronger than uncapped joints at all temperatures tested, or equivalently, to achieve a specific joint strength, capped joints require a lower bonding temperature. For example, our data suggests that a joint strength of 26.9 g per bump can be obtained at 160 °C through SAM capping. In comparison, this is not achievable for blank gold, even at 200 °C. We postulate that this significant reduction in temperature needed for bond formation is due to the passivation properties of a densely packed monolayer on gold surface. We further discuss this claim in the following paragraphs.

Since direct metal thermocompression bonding involves the formation of a solid state bond between two metal surfaces by bringing the interface to an elevated temperature and simultaneously deforming the members by applying bonding load, it is of utmost importance that the surfaces exposed for bonding to be clean. It had been reported that the presence of adventitious organic contaminants on exposed surfaces results in the necessity of high thermal/mechanical loading during bonding process.[5] We also attribute the role of temperature during bonding in providing adequate thermal energy to displace deformed contamination layer before bonding occurs.[6,7] Since our experiments show a reduced bonding temperature required for samples coated with DDT, we infer that such phenomenon may be related to surface passivation, which effectively reduces surface contaminants on gold.

Substantiating the above postulation, we measured the surface composition of two types of surfaces (uncoated gold and freshly coated C_{12} gold) over a period of time as described below. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Perkin-Elmer PHI 5600 spectrometer with a nonmonochromatized Mg $K\alpha$ radiation (2.5×10^{-9} Torr). All XPS data were acquired using analyzer pass energy of 23.5 eV for narrow scan spectra. The electron take-off angle was 45°. To monitor the relative changes to the amount of contaminants on their surfaces with time, both samples were exposed in a desiccator for a period of 0, 1, 11, and 31 days before loading into the vacuum chamber. The corresponding changes in the quantities of C 1s and O 1s elements with time are further quantified by comparing the respective peak area ratios of these elements with Au 4f. These peak areas were taken from fitted curves under the raw spectra.

Figure 2 shows the peak area ratios of O 1s/Au 4f and C 1s/Au 4f for C_{12}-coated gold, and uncoated gold respectively. The ability of thiols in removing the oxygen contaminants during solution deposition explains why the C_{12}-coated surface is much lower in O content prior to ambient exposure.[8] As the exposure time increases, there is a concurrent rise in O as well as C content on the uncoated Au surface. In contrast, the C_{12}-coated surface exhibits very low O uptake and even a slightly negative C uptake. It has been pointed out that the primary surface contaminants on surfaces consist of mainly carbon and oxygen[9,10] and several reports have documented the formation of chemisorbed CO-metal bonds on metal surfaces.[11] The simultaneous increase in the oxygen and carbon found on uncoated gold surface can thus be attributed to CO adsorption. Therefore, the low uptake of C and O found on C_{12}-coated gold must be due to an effective passivation of the surface against further surface contamination. The decrease in C content on C_{12}-coated surface with prolonged exposure is probably due to the desorption of carbon from the alkyl chains.[12]

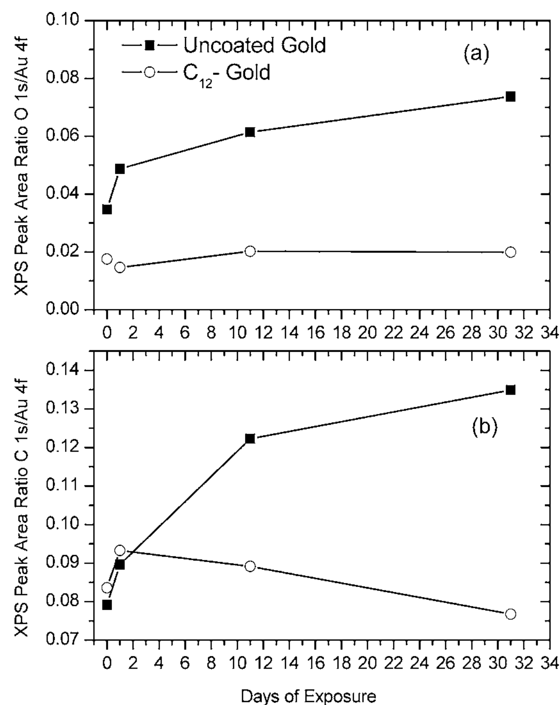

FIG. 2. XPS peak area ratios of (a) O 1s and (b) C 1s as a function of time.

Further bonding experiments were carried out to evaluate the hypothesis. We exposed UV-cleaned gold bumps and substrates as well as freshly coated DDT samples to ambient over 1 and 3 days before they were each bonded. All C_{12}-coated samples displayed enhanced tensile strength (equivalent to lower bonding temperature needed) over UV-cleaned samples as a function of exposure time. This, again, supports our hypothesis that DDT layer blocks off contaminants from gold surface. All bonding steps in this work were carried out in ambient conditions, and there was a finite time lag in temperature stabilization, as mentioned in the experimental section, which means that all samples, regardless of capping conditions, will experience inevitable environmental exposure prior to bonding. This nonzero net exposure explains why there is a net improvement in strength of capped Au surfaces over uncapped surfaces even at time of zero, as shown in Fig. 3. This underlines the extreme difficulty of maintaining a pristine clean gold surface at the moment of bonding. Interestingly, it was noted that the gain in strength relative to UV-cleaned samples was found to be more apparent for samples exposed over a longer period of time before they were subjected to bonding, shown in Fig. 3. The efficacy of SAMs in protecting gold surfaces for bonding is accentuated as unprotected gold surface gets dirtier, as consistent with the exposure results.

It is also worth mentioning that while the SAM layer behaves as an adequate coating to inhibit further surface contamination, it is imperative that this layer be sufficiently and easily displaced prior to bonding. To evaluate this, we made use of a surface-sensitive technique—surface plasmon resonance spectroscopy (SPRS)—to predict the degradation temperature of SAMs. Using an SPR system with a Kretschmann configuration, the collected angular spectrum exhibits a dip at a particular angle only at an appropriate condition (e.g., metal thickness, incident angle, etc.). This

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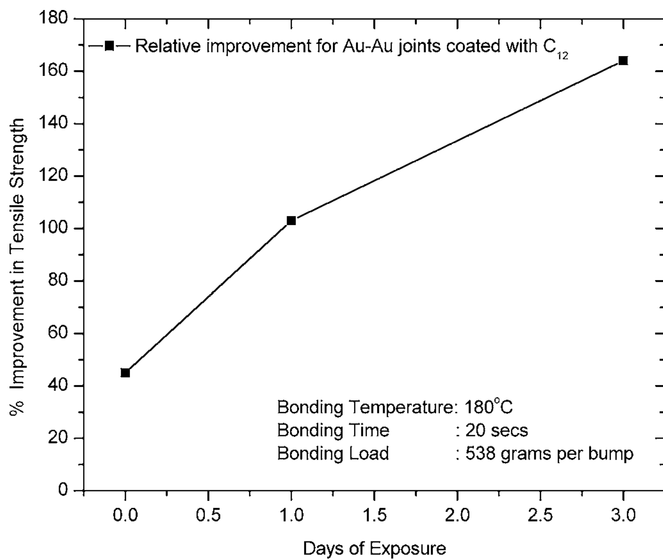

FIG. 3. Relative percentage improvement in tensile strength between DDT-coated and uncoated gold samples as a function of exposure time prior bonding

dip, known as resonant angle is very sensitive to minute variation in thickness and/or refractive index of the dielectric layer (SAMs) above the metal layer (50 nm gold) due to the extremely strong evanescent field generated at the metal/dielectric interface.[13] Figure 4 consolidates the resonant angles for a four-layer (prism/gold/C_{12}/air) and three-layer system (prism/gold/air) with respect to increasing temperature. We observed a continual reduction in the resonant angle for the four-layer system, suggesting a reduction in thickness and/or refractive index of the DDT layer. Similarly, a slight shift of the resonant condition was observed for the three-layer system, most probably due to the desorption of inevitable surface contaminants present on blank gold. Extrapolation of the two linear behaviors of the resonant angle of blank Au/air and Au/C_{12}-SAMs with temperature predicts that the monolayer will desorb completely at around 104 °C, depicted by the intersection point of the linear curves. Our approximate prediction is supported by Guo *et al.*[14] who reported that the desorption of dodecanethiol was observed at temperature above 117 °C. This complements our previous prediction that SAMs do not hinder bonding since its postulated degradation temperature is significantly below the conventional bonding temperature of about 150 °C.

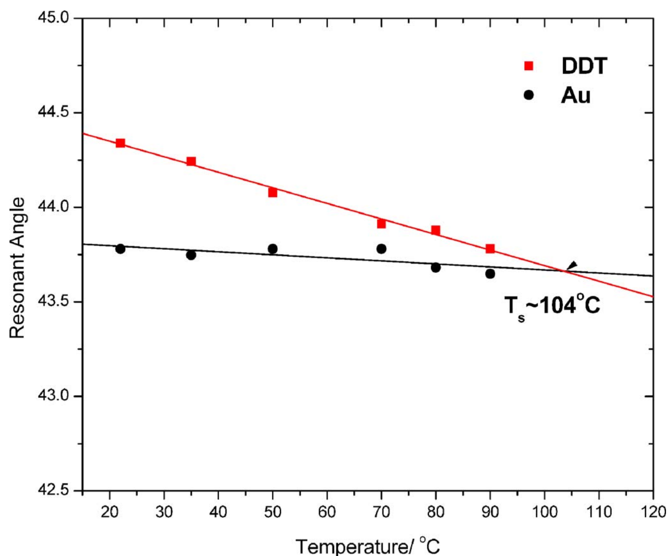

FIG. 4. (Color online) Variation of resonant behavior with respect to heating temperature.

In summary, low temperature gold-gold bonding is achieved using self-assembled monolayers. Since surface contamination is the key factor that determines the amount of bonding temperature required for a particular joint strength, we have demonstrated that with SAMs, contaminants on gold are reduced significantly. Within this additional simple bonding procedure, SAMs have a dual role, namely, to act as a passivating layer against surface contamination and to be conveniently displaced by thermal desorption at the bonding temperature.

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[1]K. Tanida, M. Umemoto, T. Morifuji, R. Kajiwara, T. Ando, Y. Tomita, N. Tanaka, and K. Takahashi, Jpn. J. Appl. Phys., Part 1 **43**, 2264 (2004).
[2]K. Tanida, M. Umemoto, T. Morifuji, R. Kajiwara, T. Ando, Y. Tomita, N. Tanaka, and K. Takahashi, Jpn. J. Appl. Phys., Part 1 **42**, 6390 (2003).
[3]Q. Y. Tong, Appl. Phys. Lett. **89**, 182101 (2006).
[4]F. Schreiber, Prog. Surf. Sci. **65**, 151 (2000).
[5]J. Jellison, IEEE Transactions on Parts, Hybrids, and Packaging **11**, 206 (1975).
[6]X. F. Ang, G. G. Zhang, J. Wei, Z. Chen, and C. C. Wong, Thin Solid Films **504**, 379 (2006).
[7]G. G. Zhang, X. F. Ang, J. Wei, Z. Chen, and C. C. Wong, J. Appl. Phys. (submitted for publication).
[8]T. Laiho and J. A. Leiro, Appl. Surf. Sci. **252**, 6304 (2006).
[9]H. L. L. Watton, A. G. Fitzgerald, and P. A. Moir, Surf. Interface Anal. **17**, 320 (1991).
[10]S. Tennyson, J. Colloid Interface Sci. **75**, 51 (1980).
[11]P. R. Norton, R. L. Tapping, and J. W. Goodale, Surf. Sci. **72**, 33 (1978).
[12]T. M. Willey, A. L. Vance, T. B. Van, C. Bostedt, L. J. Terminello, and C. S. Fadley, Surf. Sci. **576**, 188 (2005).
[13]S. Ekgasit, C. Thammacharoen, and W. Knoll, Anal. Chem. **76**, 561 (2004).
[14]Q. Guo, X. Sun, and R. E. Palmer, Phys. Rev. B **71**, 035406 (2005).

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