SAMs (self-assembled monolayers) passivation of cobalt microbumps for 3D stacking of Si chips

Lin Hou[1], Jaber Derakhshandeh[2], Silvia Armini[2], Carine Gerets[2], Inge De Preter[2], Kenneth June Rebibis[2], Andy Miller[2], Ingrid De wolf[1,2] and Eric Beyne[2]

1) Dept. Materials Engineering, KU Leuven, Leuven, Belgium

2) IMEC, Kapeldreef 75, 3001 Leuven, Belgium E-mail: lin.hou@student.keleuven.be;

Abstract

In this paper SAM (self-assembled monolayers) is used to passivate cobalt microbumps for 3D-stacking of Si chips. The SAM deposition process is optimized, using input from characterization techniques such as water contact angle measurement, ATR, AFM and XPS analysis in order to form a monolayer of Thiols-SAM on cobalt microbumps. A 3D stacked Si chips test vehicle was used to demonstrate the effectiveness of the SAM coating on cobalt bumps by measuring the electrical continuity of daisy chains.

1. Introduction

To improve the performance of electronics products such as logic and memory chips beside scaling transistor gate length, Si chips are stacked on top of each other (three dimensional ICs). This will offer a shorter interconnect therefore less power consumption and better performance. In 3DIC technology, microbumps and through-Si vias (TSVs) are being used to form electrical interconnects between the stacked chips. Copper has been used for several years as UBM (under bump metallization) for both 3D-IC and flip chip packages. However, Cu has several disadvantages such as the formation of Kirkendall voids at the interface of the bump and the Sn-solder during phase transformation from Cu_6Sn_5 to Cu_3Sn which occurs during ageing or due to electro-migration test. Furthermore, Cu has hard IMC (intermetallic compound) phases which leads to poor mechanical properties [1]. As an alternative to Cu, cobalt has better properties to be used as UBM material for microbumps. Due to its softer and single IMC phase at the interface with the Sn solder which offers void free joint formation and less stress concentration [2]. However, the main challenge for Co as UBM is that Co oxidizes very fast, which will lead to poor interconnect and wettability between the interconnected dies. To solve this problem, capping layers are used on Co UBM microbumps to passivate the Co UBM and to prevent formation of the cobalt oxides.

A self-assembled monolayer (SAM) is an organic assembly formed by the adsorption of molecular constituents from a solution or the gas phase onto the surface of solids or liquids. The structure of the self-assembled monolayers includes a head group, alkane chain and terminal group. The high affinity of thiols (head group)-SAMs for the metal surface makes it possible to generate well-defined organic surfaces as diffusion barriers and passivation layers in 3D interconnects [3]. Self-assembled monolayers as surface passivation layer for Cu-Cu direct bonding have been studied in several reports. The results showed that the self-assembled monolayers can reduce the Cu-Cu direct bonding temperature due to passivation of the Cu surface and the suppression of the oxides formation [4]. In this paper it is shown that SAM can be used to passivate the cobalt microbump and to inhibit oxides formation on the surface. Since SAM layers start to desorb during bonding above the melting point of the Sn-solder, they will not add any unwanted IMC phases at the interface after bonding. Moreover, SAM deposition processing is an inexpensive and reliable process compared with other capping layer deposition processes.

2. Experimental results

H_2 microwave plasma cleaning or commercial Microstrip 6020 solution cleaning was used to remove cobalt oxide on the microbumps prior to SAM deposition. Thiols-SAM solution (1-Octadecanethiol, Sigma-Aldrich, 98%) is prepared in a 1mM and 5mM solution of ethanol. SAM monolayers were prepared by immersion of the cobalt coupons directly into the SAM solution after pretreatment cleaning in the glovebox. After SAM immersion processing, cobalt coupons were copiously rinsed with ethanol, flushed dry under nitrogen flow and then characterized.

Monolayers on blanket cobalt coupons were characterized by static contact angle measurement and ATR to study the deposition and wettability of the SAM layer. Atomic force microscopy (AFM) was used to check the surface roughness and X-ray photoelectron spectroscopy (XPS) was used to investigate the passivation properties of SAM on cobalt samples. A test vehicle with 20um and 40um pitch daisy chains were employed to verify effectiveness of SAM on Cobalt bumps. Electrical resistance testing and scanning electron microscope (SEM) cross-section analysis were done on stacked dies.

The water contact angle measurement is one method to quantize liquid spread ability on the solid surface. The aim of the water contact angle measurement is to characterize the film formation on the surface. The original cobalt coupons (without any pretreatment) have a hydrophilic surface, which will lead to low contact angle. The contact angle of cobalt coupons with MS6020 cleaning is 54 degree and this angle could go to 52 degree with plasma cleaning. However, the hydrophobicity of the surface will increase after surface modification with self-assembled monolayers. Water contact angle results of ODT (1-Octadecanethiol) SAMs are shown in Figure 1. It is clearly seen that, for 5mM ODT SAM, the contact angle of the SAM passivated cobalt coupons reaches to 120 degree after 1h

deposition. With increasing immersion time, the hydrophobicity of the self-assembled monolayers reaches to saturation and does not increase any more. However, for a lower concentration, 1mM ODT SAM deposition, the contact angle of the cobalt surface is increasing gradually and it will reach to saturation point at 36 h immersion. The maximum contact angle can reach almost 140 degree and shows super-hydrophobicity properties after 24 h immersion. Therefore, a lower ODT SAM concentration can offer better surface modification compared with a high ODT SAM concentration. Observations by optical microscopic revealed that high concentration SAM solution would lead to surface crystal formation.

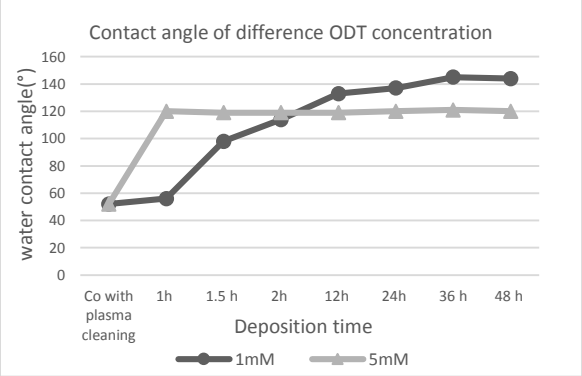

Figure1: Results of water contact angle measurement on SAM deposited on cobalt coupons

The substrate roughness has a significant influence on the SAM deposition [3]. The substrate roughness with different pretreatment cleaning have been measured by AFM. The results of AFM analysis showed that the roughness of original coupons (without any cleaning) is quite high. Pretreatment cleaning can reduce surface roughness specially microwave plasma cleaning offers a flatter substrate compared with MS6020. The RMS (root mean square) and RA (Roughness average) value of the surface roughness are displayed in Table I.

Table I Surface roughness changes before and after pre-treatment cleaning

Image statistic	Co without cleaning	Co with plasma cleaning	Co with MS6020 cleaning
Rms(Rq)	15.5nm	6.0nm	6.5nm
Ra	11.2nm	4.5nm	5.2nm

Attenuated total reflectance (ATR) has been used to analyze specific bonds by measuring the spectrum of attenuated light when the infrared beam occurs totally internally reflected between sample and ATR crystal [5]. Some specific bonds such as sp3 C–H stretch in the self-assembled monolayer structure can be detected by ATR analysis. The ATR results of 5mM ODT SAM passivated cobalt coupons with different deposition time (1h, 6h, 12h, 24h) are shown in Figure 2. It can be observed that the absorbance of C-H stretch alkanes is increases with longer deposition time, which indicates densification of the layer or multilayer formation. It can be seen that 1mM ODT SAM showed the same tendency. Another interesting observation is the peak of O-H which is also detected in ATR analysis. The absorbance of O-H peak decreases with increasing deposition time. The reason is that SAM deposition on the surface of the Co coupons will reduce the amount of H_2O which is absorbed on the Co metal surface due to hydrogen bond formation between cobalt and H_2O.

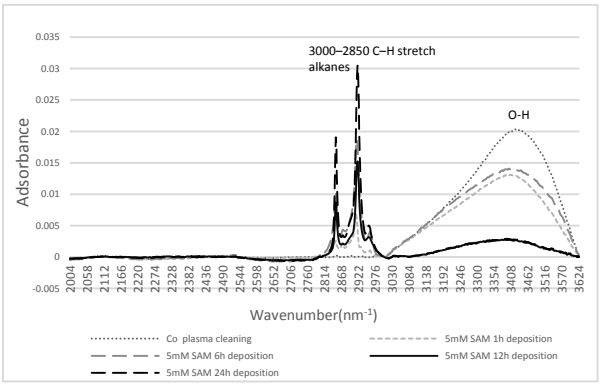

Figure2: ATR result of 5mM ODT SAM passivated cobalt coupons

The XPS results of the ODT SAM modified cobalt coupons by MS6020\plasma cleaning are shown in Figure 3. It can be seen that there is almost no cobalt and oxygen signal measured on the cobalt surface after SAM deposition, which means that cobalt UBM is passivated by ODT SAM after pretreatment cleaning. It should be noted that the MS6020 cleaned sample followed by 6h SAM deposition still shows significant amount of cobalt and oxygen signal detected on the surface compared with plasma cleaning. While these amounts are very low for the sample that had plasma cleaning and 6h SAM. This might be due to the smoother Co surface after plasma cleaning, as shown in Table I.

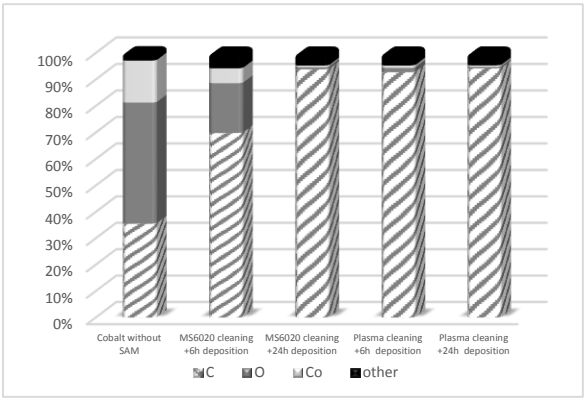

Figure 3: XPS surface analysis of SAM passivated cobalt coupons

During die to wafer TCB (thermo-compression bonding) process, the wafer will stay at 70 ℃ for around 2h therefore it is necessary to study the SAMs stability at 70 ℃ for 2h. An ideal state is that SAMs should be stable at 70 ℃ preventing cobalt bumps from oxidation but evaporate totally during bonding specific die when temperature is high enough to melt solder. After annealing the SAMs modified cobalt coupons, XPS is used to investigate the surface properties and passivation stability. It can be clearly observed that, after annealing, both cobalt and oxygen signal are detected by XPS surface analysis. It can be seen that the MS6020 cleaned cobalt samples show more oxide growth on the surface than the plasma cleaned cobalt coupons. Possibly, this is related to substrate roughness and better SAM layer on plasma cleaned surface. Therefore plasma cleaning can offer a better surface passivation compared with MS6020 wet cleaning. The result are shown in Figure 4.

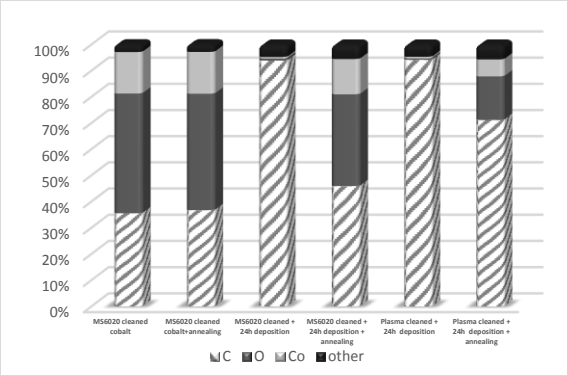

Figure 4: XPS surface analysis of SAMs passivated cobalt coupons with/without annealing

In order to verify effectiveness of SAM layer on cobalt microbumps, an IMEC test vehicle with 40 µm pitch and 20 µm pitch microbumps was used. The top die microbumps contains Cu/Ni/Sn with 5/1/3.5 µm thickness and on bottom die has 5 µm thick cobalt microbumps coated with SAM. Stacking processing is done on a Chameo thermo-compression bonder (TCB) from the Besi company. The electrical resistance of the connected daisy chains through the microbumps between top and bottom dies was measured to investigate the quality of the bonding with the SAM passivated cobalt surface. The resistance of the 40um pitch and 20um pitch daisy chains normalized to the number of bumps for each daisy chain and is shown in Figure 5. It can be seen that, for 40um pitch, 80% of samples with ODT SAM passivation, have a resistance below 20Ω which is in the expected range for microbumps resistance per joint. It should be mentioned that the back-end-of-line metal track has a major contribution to the resistance of daisy chain. From Kelvin structure measurement, it was found that resistance of one bump is in the mΩ range. For 20um pitch, 25% of samples with ODT SAM passivation, have resistance below 20Ω. It should be mentioned that without SAM deposition there was no electrical yield.

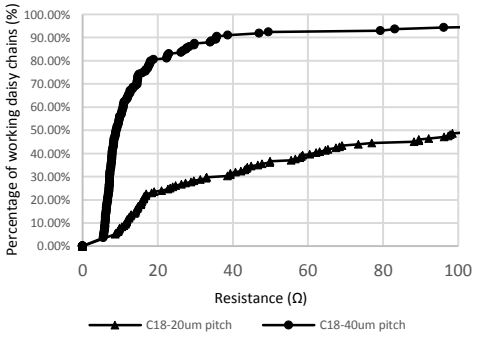

Figure 5: Measured electrical resistance of 40um and 20um pitch daisy chain per joint

To investigate the joint quality of Co-Sn interface, SEM cross section was used. The SEM images are shown in Figure 6. As can be seen, joint formation between Sn and Cu is fine and there is connection between Sn and Co. However, the Sn still does not wet the cobalt bumps in a proper way. The TCB stacking profile needs to be further improved in order to obtain full IMC formation between Sn and cobalt.

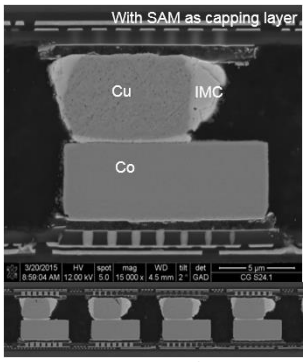

Figure 6: SEM cross section images of SAMs passivated Co UBM microbumps

3. Conclusion

Self-assembled monolayer as passivation layer on cobalt coupons was investigated using several characterization methods such as contact angle, ATR, AFM and XPS. The aim is to optimize the SAM coating conditions on cobalt microbumps such that they can be used for bonding without problems due to oxide formation on the surface. It was shown that using 1mM concentration of SAM resulted in a higher contact angle than 5mM. After cleaning, the surface roughness of bumps was reduced by factor of 3. From an ATR study it was shown that a longer immersion time results in higher alkane C-H stretch. XPS analysis showed that plasma cleaning prior to SAM coating resulted in a better passivation rather than wet cleaning. 3D Si stacks with functional microbumps daisy chains showed that 80% of the samples have a resistance in the expected range for well bonded 40um pitch cobalt microbumps, indicating that the SAM coating indeed prevents oxidation and improves the bonding quality.

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