Room Temperature Desorption of Self Assembled Monolayer from Copper Surface for Low Temperature & Low Pressure Thermocompression Bonding

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Abstract

In this paper the utility of Self Assembled Monolayer (SAM) of Propanethiol (C3) for Copper protection from oxidation and subsequent desorption of the Thiol layer from Copper surface by using cold Helium plasma has been investigated. The major bottleneck of achieving low temperature and low pressure bonding is the presence of contamination and oxidation on the Copper surface. Use of Thiol can protect the freshly deposited Copper surface from oxidation and other contamination. Removal of this Thiol layer by Helium plasma just prior to bonding can bring down the required temperature of bonding to 200^0 and pressure to 4kN. This technique can open up a whole new platform for low temperature bonding for 3D ICs.

Keywords: SAM, Thiol, Thermocompression, Helium Plasma, 3D IC

Introduction

The demand for more functionality within a single chip is growing in every decade. To be on track of Moore's law the viable option was aggressive scaling down of the device dimensions [1]. As the device dimensions has already reached to its fundamental limit scaling down of dimension is no longer a reasonable choice. It seems that a paradigm shift is necessary to satisfy the ever-growing demand of higher performance. 3Dimensional Integration can bring such possibility in reality. 3D Integration is advantageous over conventional planer integration predominantly because of its shorter interconnects which reduces RC delay thereby increasing the bandwidth. Furthermore, unlike conventional technology, heterogeneous integration is possible in 3D IC technology which is regarded as the way forward [1,2].

As precise alignment is possible in wafer-on–wafer integration, such a technique has drawn worldwide interest in the 3D Integration platform to produce high capacity memory [1, 3]. There are many advantages of using Copper as bonding medium. Apart from its excellent electrical conductivity and mechanical strength, it has better electro-migration resistance than Aluminum and is also being regularly used metallization layer in conventional CMOS process [2]. Thermocompression wafer-wafer bonding is one of the most preferred choice in the IC industry. Thermocompression bonding is better than the conventional ball grid array or micro bump techniques.

Application of high bonding pressure (3.28GPa) has been reported for Copper-Copper bonding [4]. Such a high force while bonding can cause performance degradation of underlying devices. Room temperature bonding at relatively low pressure has been reported by using Surface Activated Bonding (SAB) technique. But the stringent requirement of atomically smooth surface and UHV makes this process complex and not cost effective [5,6]. Thermo- compression bonding has drawn attention because this technique is more tolerable in regard of surface roughness and it does not require any additional CMP process step [2].

The major bottleneck of Copper-Copper thermocompression bonding is presence of surface oxidation and contamination. To protect the Copper surface from oxidation use of Self Assembled Monolayer of Alkane Thiol has been reported [7, 8, 9]. Formation of this organic monolayers is spontaneous and this is non-toxic [10, 11]. These organic monolayers have the excellent ability to remove small amount of native Copper oxide present on the Copper surface. Complete desorption of this Thiol layer just prior to bonding is mandatory because the presence of this monolayer can act like a barrier for free diffusion of Copper atoms from one wafer to other. Researchers have explored several ways of desorbing SAM. Applying high pressure of 2.58GPa Nano Structured Organic Compound can be displaced mechanically from the Copper surface [12].

Another method of application of heat (250^0C) to desorb this monolayer has also been reported [13]. But this means that below this 250^0C temperature bonding cannot be initiated. Application of formic acid to clean the surface of Copper has been reported [14]. Reports indicate the use of Ti as a capping layer on top of Copper [15]. It has been suggested that such Ti layer can protect the Copper surface from oxidation for a reasonable amount of time.

As high temperature or high pressure both are potential cause for performance degradation of sensitive CMOS devices we propose the application of Non Thermal Helium plasma for successful desorption of Thiol at room temperature and atmospheric pressure. As an inert gas He does not react with Copper and chances of forming any compound are minimal. As Non Thermal Plasma can be produced at room temperature, it can reduce the thermal budget significantly. Thus solving one of the primary challenges of thermal budget of IC industry. Non Thermal Plasma can be generated at atmospheric pressure. It does not require any vacuum condition. The degree of ionization can be controlled both precisely and accurately by varying the input power. The power required to generate the plasma was optimized in such a way that it can remove only the Thiol monolayer without attacking the Copper surface. Non thermal Plasma is an easy and efficient way to desorb the Thiol layer which can guarantee high throughput which is a mandatory criterion for wide scale application and mass production.

In this present study samples were prepared with Ti and Cu. After temporary protection of Cu surface from oxidation by using Alkanethiol, Non-Thermal He plasma was used to desorb the organic monolayer from Cu surface. Then thermocompression bonding was performed. Pre and post bonding characterization was carried out to analyze the surface morphology and bonding quality. In this regard contact angle of DI water was monitored for analyzing surface condition. Atomic Force Microscopy was used for understanding the surface roughness, Scanning Acoustic Microscopy and Cross Sectional SEM was used to analyze the bonding quality. Ultimately Microtester was used to understand the mechanical strength of the bonded samples.

The primary objective of this present study is the application of Non Thermal He Plasma to desorb the Thiol layer from Copper surface which in turn dramatically brings down the required temperature for thermocompression bonding.

The concept of room temperature desorption of Thiol from Copper surface can open up a new approach in the IC industry.

Experiment

Sample preparation: 4", (100), n-type wafers were used for entire operation. Cleaning is one of the most basic and fundamental step in every CMOS process. At first solution was prepared with H_2SO_4 and H_2O_2 with the ratio of 3:1. This solution is commonly known as Piranha and wafers were immersed in the solution for 15 minutes. All the organic residues are removed from the substrate surface after this cleaning process.

RCA stands for Radio Corporation of America. In this process two steps are involved. The first one is known as RCA 1 where DI water, NH_4OH and H_2O_2 were mixed with the ratio of 5:1:1. After heating at 80^0C the wafers were immersed and kept for 10 minutes. This process can remove the organic residues.

On the second step the ionic residues were removed. This step is commonly known as RCA 2 where DI water, HCl and H_2O_2 were mixed with the ratio of 5:1:1. After attaining 80^0C temperature the wafers were immersed for 10 minutes.

Finally the wafers were rinsed with DI water and dried with Nitrogen.

25nm of Ti and 200nm of Copper was sputter deposited. The Ti layer acts like a diffusion barrier for Copper. Before actual deposition started each target was pre-sputtered for at least 20 minutes. The sputtering system used throughout the work is AJA Int. PHASE II system. Freshly deposited wafers were immediately immersed in 1 mmol Propanethiol (C_3H_8S, SIGMA-ALDRICH) solution with ethanol. To protect the Copper sample along with the Thiol the entire system was kept in nitrogen purged dry vacuum box. Samples were kept in such neutral ambient for several hours. The Thiol has the –SH head group and CH tail group. The Carbon makes the backbone for the entire chain. The –SH head group has the excellent affinity to metals and after immersion chemisorbs on the Cu surface very quickly. The thiol monolayer remains stacked on the Cu surface due to van der Walls force. It is the presence of the Sulfur head group which makes the Cu surface hydrophobic. The application of Thiol as a temporary protection of Cu has several advantages which include the ease of preparation, it is non-toxic and it does not attack the Cu surface planarity. Instead it has got the excellent property to reduce any native Copper oxide layer from the Copper surface and bring back the pure Cu.

SAM adsorption: Contact angle of DI water droplet on the Copper surface was monitored using Goniometer. Figure 1c shows the sharp rise of Contact Angle after 2 hours of immersion. The Contact Angle study is one of the best method to monitor the surface morphology of the Copper surface which in turn confirms the SAM adsorption.

Plasma desorption : It is mandatory to desorb the Thiol layer completely from the Copper surface just prior to bonding or any other technological use like packaging. In this work indigenously designed Plasma reactor was used to create Helium plasma for complete desorption of Thiol layer.

The plasma which was produced in this work was corona discharge, non thermal atmospheric pressure plasma. Schematic of the indigenously designed plasma reactor is shown in figure 1. The reactor was 30 cm long and 1 cm thick glass tube. The inner diameter of the tube is 150mm. stainless steel discs with 2mm thickness and 100mm diameter was used as electrodes. High voltage AC transformer was used to apply the required voltage to generate the plasma.

Samples were placed in between two electrodes. The distance between two electrodes was kept 2cm. the voltage level was kept at 8kV-10kV. 50Hz frequency was used while treating the sample. The He flow rate was 280mL/min.

Surface analysis: Atomic Force Microscopy was used to monitor the relative surface roughness of the Copper surface at various stages of the operation. Roughness was tested on freshly deposited Copper surface, after SAM adsorption, and after Plasma treatment.

Bonding: Low temperature and low pressure bonding was the main interest of this present study. Samples were bonded accordingly just after Plasma treatment in the wafer bonder system (AML, UK). The bonding parameters are listed below in Table 1

Bond interface analysis: Scanning Acoustic Microscopy (Sonoscan, UK) was used to check the quality of the bonded interface. This is one of the best non-destructive methods to analyze the quality of the interface.

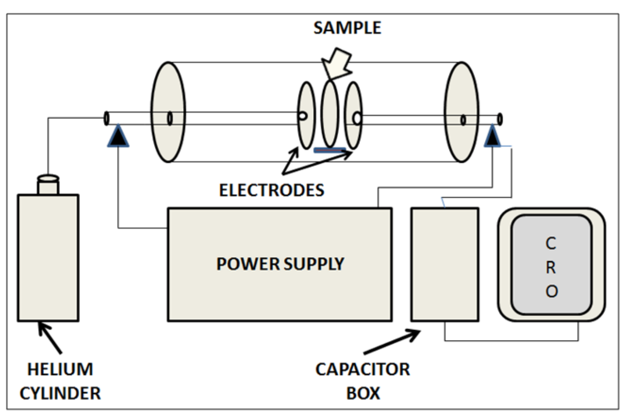
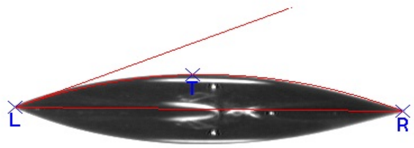
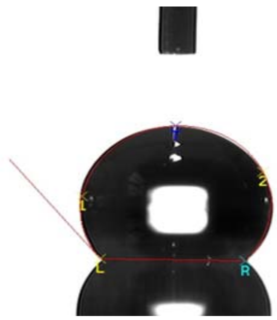


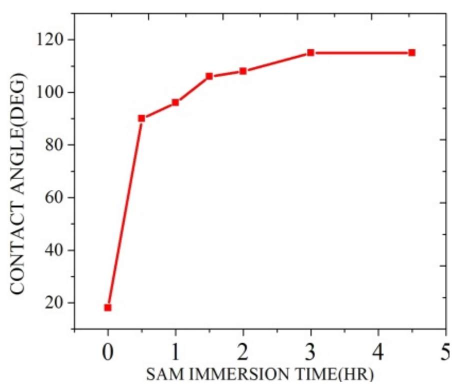
Figure 1: Schematic diagram of the Non Thermal atmospheric pressure He plasma set up.



(a)



(b)



(c)

Figure 2: (a) Contact angle of DI water droplet on the freshly deposited Cu surface is 20^0 which suggests that pure Cu surface is hydrophilic in nature. (b) After 3 hours of immersion in the Thiol solution the contact angle of the Cu surface becomes 117^0 confirming that Cu surface becomes inverted and hydrophobic due to the presence of SAM layer. (c) Contact angle of DI water on the Cu surface vs SAM immersion time suggests that sharp increment of contact angle can be observed and surface transition has taken place. After 4 hours of immersion there is no significant change in contact angle which implies that formation of SAM has become saturated on the Cu surface.

Bond strength analysis: Superior bond strength is as important as excellent electrical conductivity. Bond strength analysis indicates the mechanical stability of the bonded sample. If the mechanical stability of bonded sample is poor then it cannot sustain subsequent process steps. In this study bond strength of each sample were tested by using Microtester (INSTRON). The compressive stress was provided by one actuator. The speed of the actuator was kept at 0.6mm/min. the maximum limit of the system was at 950N.

SEM analysis: To understand the quality of bonded interface FESEM analysis was performed. This is one of the best method to understand the near atomic level condition of the bonded interface.

Results & Discussion

SAM adsorption and degradation: Figure 2a. shows the Contact angle of DI water droplet on freshly deposited Copper surface as 20^0. After 2hrs of immersion within Thiol solution this angle rises sharply and Figure 2b. shows the Contact angle to be 117^0. As pure Copper is hydrophilic in nature, such hydrophobicity after SAM immersion suggests the complete adsorption of Thiol on the Copper surface. Figure 2c. shows the relative change of Contact Angle of Copper surface versus SAM immersion time. It suggests that after 2 hrs of immersion there is no significant change of contact angle and SAM adsorption reaches to saturation level. This is because after 2hrs of immersion the entire Copper surface gets chemisorbed by Thiol layer and no space is left for further adsorption.

Cold Plasma desorption: Just prior to bonding the SAM layer is to be completely desorbed from the Copper surface. For this cold Helium plasma was used. It has been observed that samples exposed at 10kV and for 15 minutes with cold plasma ensures complete desorption of Thiol layer without damaging the Copper film.

Figure 3 shows the sharp decrement in contact angle after 10kV of plasma treatment. Figure 3 shows that contact angle is falling to 35^0 from initial 117^0 after plasma treatment. This is a clear indication of complete removal of SAM layer from Copper surface.

The slight difference in between freshly deposited Copper contact angle and plasma treated Copper contact angle is due to presence of nominal amount of Carbon on the Copper surface which is natural after prolong exposure of SAM in ambient. This complete and quick removal of SAM can enhance the throughput compared to other desorption methods like thermal desorption which requires considerable longer time.

Table 1: List of all the bonding parameters

Bonding temperature	Bonding force	Time	Vacuum
200^0C	4kN	1.5hr	$5*10^{-6}$ mbar

Surface analysis: One of the major criteria of successful thermocompression bonding is the smooth Copper surface.

As chances exist that after plasma treatment the Copper surface might get damaged and this might affect the bonding quality AFM was used to monitor surface roughness at different stages of experiment. It has been observed that the roughness of fresh Copper surface as 1.99nm. The roughness after plasma treatment is 1.46nm which is even better than fresh Copper surface. The roughness of Copper after SAM immersion to be 2.46nm.

Bond interface analysis: Scanning Acoustic Microscopy is one of the best non-destructive methods to analyze the bonded interface. Figure 4 depicts the bonded interface image achieved from Acoustic Microscope. It shows some of the white spots which were caused by voids.

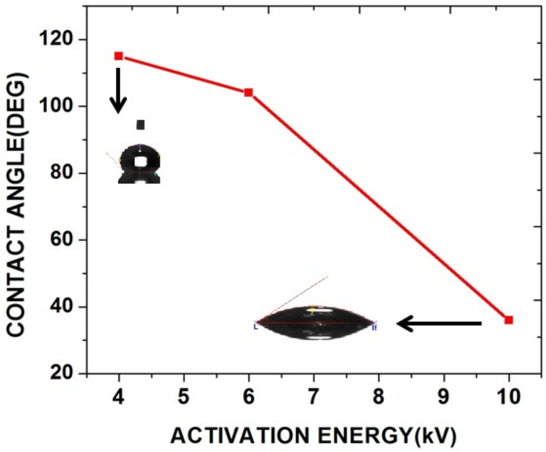


Figure 3: Decrement of contact angle with enhanced plasma activation energy. Plasma produced at 4kV is not sufficient to desorb Thiol layer. 10kV is sufficient for total desorption

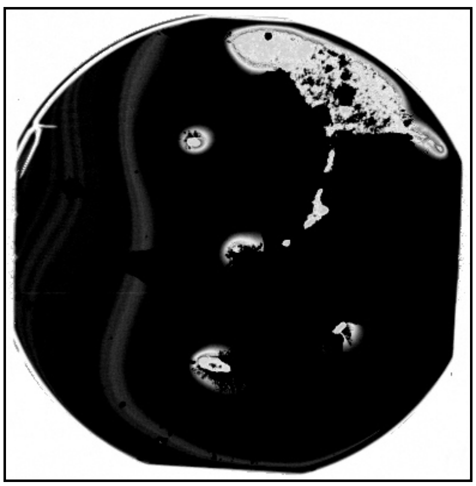


Figure 4: Bonded interface by Scanning Acoustic Microscopy (Sonoscan). 100MHz transducer scanning shows dark regions as reasonably good bonding. White spots are caused by voids due to Carbon particles

SEM analysis: Figure 5 depicts the bonded interface monitored by Scanning Electron Microscopy. The scan size of the SEM image of 5 was kept at 100nm. Figure 4 does not show any clear and distinguishable interface line which suggests that Copper atoms have diffused freely from one wafer to other wafer. Such free diffusion is the result of surface clarity which was ensured by Thiol protection.

Bond strength analysis: Figure 6 shows the bond strength of the sample bonded after complete desorption of SAM from Copper surface. The achieved bond strength was 799N which is equivalent to 145MPa.

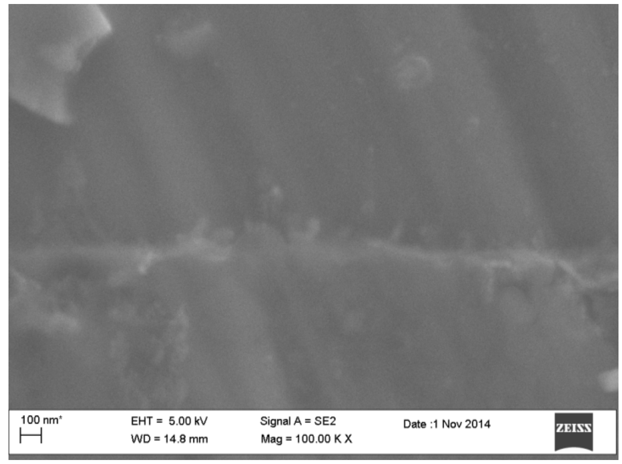


Figure 5. SEM image of bond interface (sca n size 100nm). Absence of any clear interface suggests excellent interdiffusion

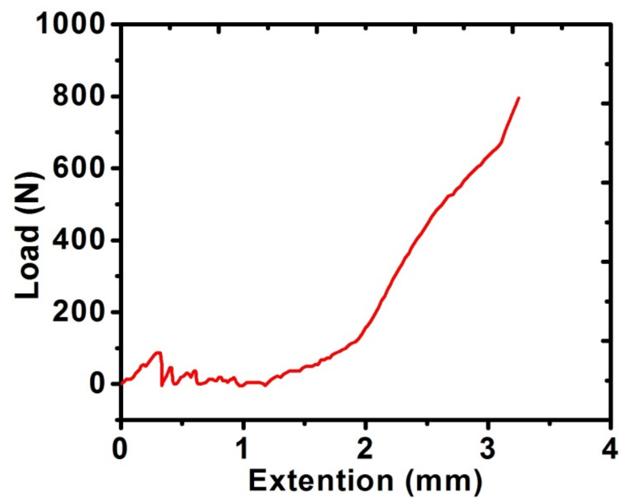


Figure 6: Bond strength of bonded sample with 1cmX 1cm area. Maximum 800N load (equivalent to 145MPa) was endured by the sample

Conclusion

Low temperature bonding of Cu interconnects in 3-D ICs is requirement but hindered by surface contamination and oxidation of Cu surface. Pure Cu surface has been protected from oxidation by using self assembled monolayer of Propanethiol. Surface become hydrophobic from hydrophilic and observed by change of contact angle of surfaces at different steps indicates adsorption of SAM layer from Cu surface. Further most importantly SAM layer has been desorbed using cold helium plasma at room temperature. Secondly the surface of the freshly deposited Copper and the Copper surface after Plasma desorption treatment has been compared using Atomic Force Microscopy (AFM) and found that after desorption of SAM the surface become even smoother. The contact angle analysis will show the adsorption and desorption of SAM layer on Copper surface. Since the CA after desorption become lower than the freshly prepared CA of wafer, due to surface become even cleaner. Further metrology like XPS, Raman spectroscopy will give more light to surface analysis.

Protection of Copper surface using SAM will minimize the possibility of forming Copper oxide. Cold plasma desorption helps in getting back the clean and pure and even smoother Copper surface on which bonding has been done at relatively lower temperature of 200^0C which is instrumental of the success of 3-D IC technology

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