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# Cu-Cu thermo compression wafer bonding techniques for micro-system integration

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Copper (Cu) is used as an interconnect material in many applications owing to its high thermal, electrical conductivity and excellent electromigration resistance. Though this material has many advantages, the main drawback is that it gets oxidized on exposure to air. Thermo-compression bonding is a wafer bonding technique that uses metal layers for heaping wafers, which aids in attaining outstanding electrical conductivity without weakening the mechanical properties. The adsorbed oxide layer hurdles the proper bonding to happen between the wafers. In order to enhance the diffusion between the metal layers, the copper oxide layer should be removed which necessitates the requirement of high temperature, pressure, long bonding time and the inert gas atmosphere throughout the Cu-Cu thermo compression wafer bonding process. Simultaneous application of high temperature and pressure for a long time leads to the deterioration of the underlying sensitive components. This paper aims to present several techniques such as surface treatment, chemical pretreatment, surface passivation, crystal orientation modification, stress gradient in the thin film and formic acid vapour treatment which are used in order to avoid the deterioration of underlying sensitive devices and to obtain a proper bonding between the wafers at low temperature and pressure.

Keywords: Thermocompression bonding, Surface treatment, Surface passivation, Formic acid vapour treatment

## **1** Introduction

Micro-Electro-Mechanical-Systems (MEMS) Technology plays a remarkable role in micro-systems as actuators and sensors. To enhance the reliability of MEMS devices, the functionality, hermetic packaging is required<sup>1</sup>. Specifically, wafer-bonding technology has gained more interest because it offers an additional degree of manufacturing flexibility with hermetic packaging<sup>2</sup>. Since Wafer level bonding using metallic thin films enhances both electrical interconnection and vacuum sealing, it is mainly useful for wafer-level MEMS packaging<sup>3</sup>. Metal-Metal thermo compression wafer bonding is an empowering technology for heterogeneous Microsystem integration of MEMS and three-dimensional integrated circuits (3D ICs)<sup>4</sup>. Apart from allowing a mechanically steady bonding, the metal bonding also guarantees high electrical, thermal conductivity and supplies efficient vacuum sealing for MEMS devices<sup>5</sup>. Metal-to-Metal bonding is having advantageous properties as it utilizes metal layers for stacking wafers, which benefits in accomplishing excellent

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electrical conductivity without negotiating on the mechanical properties. Among all the acceptable materials for bonding medium. Cu is the material of choice owing to its excellent electrical, thermal conductivity, mechanical strength, Complementary Metal Oxide Semiconductor (CMOS) process compatibility and impressive electromigration resistance<sup>3,6</sup>. Thermo compression bonding requires the concurrent application of temperature and pressure under vacuum environment for bonding two individual Cu layer deposited wafers<sup>7</sup>. The thermo compression bonding as shown in Fig. 1 takes place by means of atomic contact, diffusion and grain growth at the metal layer interfaces due to the application of heat and pressure<sup>8</sup>.

In the following sections the bonding parameters which affect the bond quality have been discussed. Since the bonding at high temperature can damage the underlying layer, it will not be suitable for CMOS integration. Hence there is a necessity of low temperature bonding. Different methods proposed by various researchers to achieve Cu—Cu thermo compression bonding at low temperature are discussed and summarized in this paper.



Fig. 1 — Metal-metal thermo compression bonding.

Influence of bonding parameters over Cu-Cu thermo compression bonding

The bonding parameters such as temperature, pressure, bonding time, chamber ambient, annealing time, surface condition of the wafers and oxide layer on metal layer play a major role in Cu-Cu thermo compression bonding<sup>9</sup>. The influence of each parameter is described in detail below.

#### **Bonding temperature**

Bonding at higher temperature enhances the diffusion and grain growth tendency of copper atoms in two bonded layers so that proper bonding can be achieved between the wafers. The native oxide layer and contaminants that are present on the surface acts as a diffusion barrier so that there is a greater necessity of higher temperature and pressure for the bonding to occur. Above 200°C, the native oxide layer that is formed on the Cu surface turn out to be thermodynamically unstable and allows diffusion of Cu atoms during the bonding process which escalates the grain growth at the bonding interface resulting in proper bonding between wafers<sup>10</sup>. In this case, a temperature of 400°C or 350°C with longer anneal period is required to attain a strong bonding quality<sup>11</sup>. However, bonding at higher temperature causes the deterioration of underlying temperature sensitive layers. Hence the bonding temperature value should be selected based on the withstanding ability of the underlying layers.

#### **Bonding pressure**

At the early stage of the bonding, the bonding pressure plays a key role in bringing the two wafer surfaces into intimate contact to allow the interdiffusion of atoms between different layers. According to the size and thickness of the wafers, the bonding pressure should be selected. Thus, adequate bonding pressure is an essential parameter for successful bonding<sup>11</sup>.

#### **Chamber ambient**

The main advantage of performing bonding at vacuum is the avoidance of particles in the atmosphere anchored to the surface. The vacuum also helps in removing oxygen, which is the main reason for copper oxidation. As copper oxide is harmful to achieve good bonding quality, it has to be eliminated before the bonding can occur between the wafers. Therefore, in order to acquire the finest quality of bonding, nitrogen purge in the chamber prior to bonding in order to remove oxygen is recommended. Hence, the chamber ambient should be maintained in a vacuum environment as low as possible<sup>11</sup>.

#### **Bonding time**

Bonding duration is another important parameter for successful bonding to take place. It plays a major role when the bonding temperature is not sufficient enough. A long time of bonding bids sufficient time for inter-diffusion of Cu atoms and allows the sufficient grain growth at the interface to complete the bonding, even though their energies are low. Most of the cases the optimum duration that are provided for proper bonding are 30 min to 60 min<sup>11</sup>.

#### Anneal

Post bond annealing enhances the inter-diffusion which causes the enlargement of grains upto 500nm, hence it is required for improving the bond quality<sup>10</sup>. In most of the cases, annealing and bonding temperature are similar and the highest temperature is considered to carry out this process. Annealing is recommended when the bonding temperature is 300°C or above<sup>11</sup>.

## Surface condition

Surface cleanliness before proceeding for bonding is very important. The impurities presented on the surface, act as a barrier for two surfaces to interact and for Cu atoms to diffuse. Thus, under the equal bonding condition, if the wafer surface is not clean, it is challenging to attain exceptional bonding quality. Hence, a standard cleaning process should be employed before proceeding for bonding to get a proper surface, which is free from contaminants<sup>11</sup>. In addition to this, the surface roughness of the Cu plays a crucial role in achieving high-quality Cu-Cu bonding. If the surface is not flat then it leads to the formation of voids and unstable grain growth throughout the bonding and may require higher pressure and longer duration to arrive at the initial point of the bonding  $process^{12}$ .

## Oxide removal

Oxides are formed on the Cu surface in the atmosphere subsequent to its deposition over the substrate. Dense oxide layer acts as the obstacle for the bonding process and degrades the bonding quality. By treating with different reducing agents, we can achieve oxide free content on the surface. The oxide as Methanol, reducing agents such Ethanol, Isopropanol, tertbutanol, Butaldehyde, Acetone, Sulfuric acid, Formic acid, Hydrochloric acid, Acetic acid and Citric acid can be employed to remove the Copper oxide on the surface prior to bonding<sup>13</sup>. Though the surface is cleaned with the reducing agent there is still the possibility of re-oxidation of metal layer to take place before the bonding due to delay in subjecting them into wafer bonder. In some cases, it can be avoided by starting the bonding process immediately after cleaning without exposing it to the atmosphere<sup>11</sup>.

By considering all the above-mentioned bonding parameters, several methods are in use to achieve high-quality Cu-Cu bonding. In order to overcome the disadvantages caused by high temperature, pressure application, it is vital to carry out the Cu-Cu thermo compression bonding process at low temperature and pressure.

## 2 Low-temperature Cu-Cu bonding techniques

The oxide layer formation increases the necessity of high temperature and high-pressure application which further leads to poor performance and damage of the underlying sensitive devices<sup>14-17</sup>. Thus, there is a solid requirement for low pressure and lowtemperature Cu-Cu steady and unfailing bonding. Therefore, various techniques are discussed in this paper which can help to carry out the Cu-Cu thermo compression bonding at low temperature and pressure.

The low-temperature Cu-Cu bonding techniques include surface activated bonding (SAB), surface passivation of Cu using Self Assembled Monolayers (SAM) and surface passivation using ultrathin passivation layers, crystal orientation modification, formic acid vapour treatment and stress gradient in the thin film. The advantages and disadvantages of each technique is discussed in detail below.

## 2.1 Surface activated bonding

Some researchers have suggested a procedure to eliminate the oxide layer on the Cu surface preceding to room temperature Cu-Cu surface activated bonding (SAB)<sup>18,19</sup>. In this process, the specimens are treated with plasma or an ion beam in vacuum to take away contaminants so that the activation of surfaces can happen, then strong direct bonding can occur between the surfaces<sup>20</sup>. Usage of Argon (Ar) ion beam creates an oxide free Cu surface on which SAB performed under ultra-high vacuum (UHV) at low thermal stress even at room temperature<sup>21</sup>. Ar plasma treatment not only eliminates oxide and other impurities but also activates Cu surface for room temperature bonding<sup>21-23</sup>.

However, the Cu surface cleaning/activation by the use of high energetic Ar bombardment to activate Cu surface creates damage of the wafers prior to bonding which will further increase surface roughness. In order to avoid these issues, Chemical Mechanical Polishing (CMP) step has been recommended proceeding to room temperature bonding<sup>24-25</sup>. A Cu surface of CMP-processed with less than 0.5 nm RMS surface roughness can be bonded directly t room

temperature without any pressure requirement<sup>26,27,28</sup>. But additional CMP step makes it complicated and costly. Suga and coworkers have proposed a new method, which involves activation of Cu surface using fluorine-containing plasma before the room temperature Cu-Cu bonding. In this technique, activation of the Cu surface is performed in a reactor by O<sub>2</sub> or  $[O_2+CF_4]^{29,30}$ .

The main shortcoming of this activation technique is the formation of a quick oxide layer over the Cu surface due to the presence of oxygen in the gas which is used for the creation of plasma.

## 2.2 Based on chemical pretreatment

A group of researchers had proposed a technique in order to remove the native oxide on the Cu surface by employing different pre-bond cleaning treatments via wet chemistry. The wet cleaning involves the use of oxide reducing agents such as citric acid<sup>31</sup>, acetic acid<sup>32,33</sup>, hydrochloric acid<sup>11,34</sup>, sulfuric acid<sup>35</sup>, Methanol, Ethanol, Isopropanol, Tertbutanol, Butaldehyde, Acetone<sup>35</sup>, Formic acid<sup>35</sup> and also some other combinations. Table 1 summarizes about the bonding parameters and bond strength for different chemical pretreatments.

The Cu surface oxide reduction by using HCl is shown in equation below<sup>11</sup>:

$$\begin{array}{l} Cu_2O(s) + 8Cl^- + 2H^+(aq) \rightarrow 2CuCl_4^{2-}(aq) + \\ H_2O(l) + 2e^- & \dots (1) \end{array}$$

$$\operatorname{CuO}(\mathrm{s}) + 4\operatorname{Cl}^{-} + 2\operatorname{H}^{+}(\mathrm{aq}) \to \operatorname{CuCl}_{4}^{2-}(\mathrm{aq}) + \operatorname{H}_{2}\operatorname{O} \dots (2)$$

The native Cu oxide can also be eliminated via acetic acid solution and the corresponding equation is shown in equation below<sup>33</sup>.

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$$CuO + 2CH_3COOH \rightarrow Cu(CH_3COOH)_2 + H_2O$$

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$$Cu_2O + 4CH_3COOH \rightarrow 2Cu(CH_3COOH)_2 + H_2O + H_2$$
... (4)

The reduction reaction with Methanol<sup>35</sup> is shown in equation below:

$$Cu_2 0 + CH_3 0H \rightarrow 2Cu + H_2 0 + ...(5)$$

The reduction reaction with Ethanol<sup>35</sup> is shown in equation below:

$$Cu_2O + C_2H_5OH \rightarrow 2Cu + H_2O(g) + CH_3CHO$$
... (6)

The reduction reaction with formic acid<sup>35</sup> is shown in equation below

$$Cu_2O + HCOOH \rightarrow 2Cu + H_2O(g) + CO_27)$$
 ... (7)

The prolonged immersion of Cu interconnect sample to the acidic medium such as sulfuric acid, hydrochloric acid, acetic acid and citric acid causes degradation of the performance of underneath active devices. Hence, this technique is not preferable to modify the Cu surface as per standards of the CMOS industry.

## 2.3 Bonding using passivation mechanisms

A strong Cu-Cu bonding between the wafers can be achieved by appropriately passivating the Cu surface. Numerous methods are in effect to passivate the Cu surface in order to protect from oxidation.

#### 2.3.1 Using metal passivation

The choice of passivation layer critically depends on its ability to allow Cu beneath it to diffuse through the layer. Optimizing the deposition conditions is the key for achieving a passivation layer that can perform

Table 1 — Summary of Cu-Cu thermo-compression bonding with different chemical pretreatment.										
Chemical Pre-treatment	Temp (°C)	Pressure (bar)	Vacuum (mbar)	Bonding Time	Characterization Result	Reference Paper				
combination of citric acid and forming gastreatment.	175	17 bar	-	30 min	C-SAM measurements, razor blade tests and XTEM images of the interface a high-quality Cu joint	[3]				
acetic acid solution held at 35°C for 1 min, 5 min, 10 min	350	25 bar	1.333X10 <sup>-3</sup>	60 min	Interfacialadhesion energies 0.29 J/m2, 1.28 J/m2,1.64 J/m2, 1.17 J/m2 respectively	[33]				
1.1 of H <sub>2</sub> O:HCl for 30 sec	400	4 bar	$1.33 \times 10^{-7}$	30 min		[11]				
Piranha solution (H2O2:H2SO4=1:3)	250, 300 & 350°C	3 bar	$2.5 \times 10^{-4}$ mbar	60 min	The best hermeticity is observed for the cavities sealed at 350 C.	[32]				

... (3)

the dual role of passivating the surface and reducing the Cu surface roughness.

Some researchers had proposed co-sputtered Cu/Ti (Titanium) as bonded interconnects for 3D IC integrations<sup>36,37</sup>. A new bonding procedure by means of Ti as a passivation layer on the surface of Cu at 180°C was reported by Hung<sup>38</sup>. A sequential sputter deposition of 20 nm Ti, 165 nm Cu and an ultra-thin Ti film was carried out on the wafers using sputtering system. Ti layer beneath Cu acts as adhesive layer between Si and Cu. The top ultra-thin layer acts as passivation layers and its thickness is varied in order to figureout the optimum thickness of the same required for passivation as well as low temperature, low pressure wafer to wafer bonding as shown in Fig. 2.

By using Auger spectroscopy, the inter-diffusion behaviour of Cu through Ti passivation layer was clarified<sup>39</sup>. In comparison, Ti vacancy volume (75.48 bohr<sup>3</sup>) is more than Cu atomic volume (72 bohr<sup>3</sup>) and Cu has lower activation energy at the surface<sup>40</sup>. Thus, Cu has a tendency to diffuse through the Ti vacancies towards the bonding interface. When



Fig. 2 — Diffusion behaviour and the structure of co-sputtered Cu/Tibonded interconnected under thermo compression bonding<sup>43</sup>.

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two wafers having Ti as a passivation layer on the Cu surface when brought into contact, the un-oxidized Cu atoms will diffuse through the Ti layer resulting in the formation of Cu-Cu wafer bonding.

The thickness of the Ti layer plays a noteworthy part during the bonding process. While thicker Ti layer can protect Cu surface from oxidation it decreases the diffusivity of Cu atoms in Ti that eventually leads to the requirement of high-pressure application during bonding. Alternatively, a very thin Ti film cannot passivate the Cu surface properly. Hence, the optimum thickness of the Ti layer is required to passivate the Cu surface allowing the Cu atoms to diffuse through Ti and initiate the bonding process at very low pressure and temperature. The effect of passivation layer thickness on Cu-Cu bonding strength and quality is demonstrated by Panigrahi et al.<sup>41,42,43</sup>.

The disadvantage of using Ti as a passivation layer is it becomes oxidized after a while and it hinders the diffusion of Cu atoms across the bonding interface which results in making the process unfeasible. Since Oxidized Ti inside the bonded layer may increase the specific contact resistance, there is a great necessity for passivation material that does not undergo oxidation for a protracted amount of time and also compatible for CMOS process<sup>44</sup>. The preferred materials for surface passivation are those which are not get oxidized at room temperature and also should be compatible with CMOS damascene process. Table 2 summarizes about the bonding parameters and bond strength for different metal passivation layers.

Cu-Cu bonding with Palladium (Pd) as the passivation layer at 150 °C provides greater electrical performance compared to Ti passivation as shown in Fig. 3<sup>45</sup>. In addition, reliability assessments such as temperature cycling, current stressing, and unbiased highly accelerated stress tests have been verified

Table 2 — Summary of Cu-Cu thermo-compression bonding with different metal passivation.								
Passivation layer	Temp (°C)	Bond Pressure(bar)	Chamber Vacuum (mbar)	Bonding Time (min)	Bond strength (MPa)	Contact Resistance (Ohm-cm2)		
Pd (10nm)	150	19.1	$1.3 \times 10^{-6}$ to $9.3 \times 10^{-3}$	50		2.0 x 10 <sup>-7</sup>		
Constantan (2 nm)	150	4	$10^{-4}$	50	200	2.0 x 10 <sup>-8</sup>		
Manganin Alloy (3 nm)	150	5	-	50	186	1.45 x 10 <sup>-7</sup>		
Ti ( 5–10-nm)	180	19.1	$1.3 \times 10^{-6}$ to 9.3 ×10^{-3}	30–50.				
Ti (3 nm)	160	2.5		50				
Ti (3 nm)	175	2.5	$4.0 \times 10^{-2}$		190			

along with inter-diffusion behaviour. The metal-based passivation techniques that are reported will not only aid in decreasing bonding temperature to 200°C but also provide reliable and superior Cu-Cu bonding.

Since Constantan which is a copper– nickel alloy gets oxidized only at temperatures more than 350 °C and no oxidation will happen at room temperature and also CMOS compatible, it is a better choice than Ti for passivating the Cu surface. A little thicker film of constantan is deposited and later it the desired precise thin layer of constantan (2 nm) is achieved by using chemical mechanical polishing. This ultra thin layer of constantan is not only to protect Cu from oxidation but it also reduces the surface roughness to about 0.7 nm, which enables Cu–Cu bonding at low temperature.

Manganin, which is a Cu rich metal alloy and has very low contact resistance acts as a passivation layer over Cu surface for achieving low temperature thermo compression bonding also, be achieved at  $150 \text{ °C}^{46}$ . Since Manganin is a Cu rich alloy, it is CMOS damascene compatible and can be easily integrated with in-line CMOS process flow.

Low contact resistance at the Cu–Cu bond interface is very important for good bonding as it directly affects the performance of integrated circuits. The specific contact resistance is high in case of titanium passivation layer as compare to Palladium and Constantan and Manganin as shown in Fig. 4<sup>47</sup> and Fig. 5<sup>46</sup>.

# 2.3.2 Bonding using SAM passivation

A noncorrosive method to passivate the Cu surface with a self-assembled monolayer (SAM) of alkanethiol and its removal prior to the bonding was proposed by Tan et al.<sup>48</sup>. Using SAM to protect the Cu surface would be a beneficial solution to carryout bonding at low temperatures. SAMs are organic assemblies that adhere to the surface of metal oxides or metals creating a highly well-organized and compactly packed monomolecular layer, which not only acts as a protection layer on the Cu surface but also augments the efficiency of passivation<sup>49,50,19</sup>. SAM formed by linear alkane-thiol atoms (CH<sub>3</sub>- $(CH_2)_{n-1}$ -SH, n= number of carbon) is freely absorbed onto the Cu surface. The methyl (-CH<sub>3</sub>) tail makes the surface hydrophobic.

This self-assembled monolayer (SAM) as a passivation coating is a cost-effective solution for low temperature bonding. SAMs are organic assemblies that attach to the surface of metals or metal oxides and form a densely packed mono molecular layer. The



Fig. 3 — Comparison of electrical characteristics of bonded Cu interconnects with Pd and Ti passivation<sup>45</sup>.



Fig. 4 — Electrical characteristics of bonded Cu interconnect with constantan passivation<sup>47</sup>.



Fig. 5 — Electrical characteristics of bonded Cu interconnect with manganin passivation<sup>46</sup>.

thickness of SAM coating in general is of few nanometers but it can protect Cu against oxidation for more than three weeks when stored at low temperatures.

Metals are deposited consecutively in a sputtering chamber for 75 nm of Ti as Cu diffusion barrier and

100 nm of Cu. As-sputtered, Cu coated wafers are immediately immersed into the solution of 1-Hexanethiol 95%. The alkane-thiol is dissolved in ethanol to a concentration of 1 mM and stored in nitrogen-purged dry box. After the specified time, Cu wafers are taken out and rinsed with copious amount of ethanol to remove the unabsorbed molecules and blown dry under nitrogen gas<sup>19,51</sup>. Cu wafers are aligned face to face, separated with spacers, and loaded into the bonding chamber. Before bonding, an in-situ ambient anneal is initiated in inert N2 (250°C, 30 min) to induce SAM desorption to recover the clean Cu surfaces<sup>52</sup>. Then the tool pressure is applied in evacuated bonding chamber is then evacuated and Bonding is performed at 250°C for 1 hr.

Nevertheless, complete elimination of the SAM layer may require temperature near to 250°C via annealing. This SAM removal process has to be done in situ in the inert gas atmosphere or vacuum to avoid Cu surface re-oxidation<sup>51</sup> as shown in Fig. 6. This high-temperature removal is a key restraint to use additional reduction of bonding temperature. For whole removal of the SAM proceeding to Cu-Cu bonding at room temperature can be achieved by using non-thermal Argon plasma treatment and bonding can be done at 200 °C<sup>53</sup>. However, SAM removal using this method, there is a chance of Cu surface re-oxidation.

# 2.4 Bonding by using formic acid vapour treatment

Wenhua Yang *et al.*<sup>55</sup> had proposed a technique in which formic acid vapour is used as in situ treatment to avoid the oxidation of the Cu surface. Generally, wet treatment of formic acid solution is utilized for the reduction of Cu surface oxide. However, the wet treatment process is not so effective for the low-temperature Cu-Cu thermo compression bonding due to reoxidation of the Cu surface when it is transferred to the bonding chamber after formic acid solution treatment<sup>54</sup>. In order to overcome this reoxidation problem, formic acid vapour in situ treatment process is employed. In this process, the oxide layer that is adsorbed on the Cu surface can be removed inside the bonding chamber s shown in Fig. 7<sup>55</sup>.

This setup includes a formic acid vapor generation unit (also called as formic acid bubbler) and bonding chamber with low vacuum as shown in Fig. 7. Formic acid vapor is generated in formic acid solution containor through importing Nitrogen (N<sub>2</sub>) gas into formic acid solution. A mixture of formic acid vapor



Fig. 6 — SAM application as a passivation layer on Cu surface to enhance bonding at lower temperature (a) a pair of Si wafers with Cu metallization, (b) immersion into alkane-thiol solution for SAM absorption and (c) pre-bonding SAM removal by temperature and bonding<sup>52</sup>.



Fig. 7 — Schematic diagram of bonder with formic acid vapor generation  $unit^{55}$ .

and  $N_2$  is introduced to the chamber by pipe and pass through the nozzle for treating Cu surface before bonding. HCOOH molecules adsorb, decompose, and react with oxide layer on Cu surface at setting temperature by heating up the stage. After formic acid vapor treatment, the formic acid gas is stopped, and the nozzle is moved away from the position between two sample stages.  $N_2$  gas is continued to fill in chamber to form  $N_2$  cycle, which can protect cleaned Cu surface, preventing surface reoxidation. Finally, Cu/Cu direct bonding is conducted at low temperature (200 °C) in  $N_2$  atmosphere through a contact force loading from the down stage.

The formic acid reduction process<sup>56</sup> can be perceived as shown in equation below:

$$\text{HCOOH} \rightarrow \text{HCOO(ads)} + \text{H}^+ + \text{e}^- \qquad \dots (8)$$

Formic acid was noticed to dehydrogenate and accumulate as formate on the surface of the metal. Dehydrogenated formic acid reacts with metal or metal oxide as mentioned in equation below:

$$HCOOH + 2M_{(s)} \rightarrow M - H + M - OOCH \qquad \dots (9)$$

 $M - OOCH \rightarrow M - H + CO_2 \qquad \dots (10)$ 

 $M - H + M - H \rightarrow H_2 + 2M \qquad \dots (11)$ 

The  $H_2$ ,  $CO_2$  & CO gases evolved during the reaction might be supportive for the reduction of the Cu oxide and the decomposition of capping molecules.

$$Cu_2 O + 2H_{(q)} \rightarrow 2Cu + H_2 O_{(q)}$$
 ... (12)

When compared to other techniques this treatment plays a major role due to the adsorption and reaction tendency of the formic acid on the surface of metals<sup>57-59</sup>. Moreover, Cu surface roughness is slightly affected by long-time formic acid treatment<sup>60</sup>. Some of the disadvantages of this treatment are it causes stains on the surface of Cu<sup>56</sup>, requirement of formic acid bubbler which is costly to create forming gas. Moreover, substrate damage occurs because of corrosion of metal is also a problem caused by the purging of formic acid vapour during the process<sup>61</sup>.

## 2.5 Bonding by texturing Cu crystal orientation

The Cu surface diffusion coefficient on <111> oriented plane is quicker in comparison with any other oriented plane at the bonding interface as reported by Agarwal *et al.*<sup>57</sup>. Manganin, which is a Cu rich metal alloy acts as a passivation layer over Cu surface and it inherently enhances Cu (111) plane orientation at the interface. Hence, high-quality consistent bonding can be achieved at  $140^{\circ}C^{21,46}$ . Also, nanotwinned Cu surface can be formed at the interface in order to enhance the diffusion capability during thermo compression cycle so that succeeding

bonding can be achieved at  $150^{\circ}$ C. When an oriented nanotwinned Cu is deposited with the (111) twin plane parallel to the free surface, A direct bonding can be achieved at low temperature down to 150 °C. For achieving this, the important requirement is that at least one of the Cu pieces to be bonded must have a (111) surface. If both Cu pieces are <111> oriented and nanotwinned Cu, the bonding can be carried out at a faster rate<sup>58</sup>.

## **3** Conclusions

In this review, the different techniques that can be used in low-temperature Cu-Cu bonding are discussed, which is essential requirement is for 3D ICs and heterogeneous integration applications. Numerous insitu and ex-situ techniques such as surface cleaning, surface passivation, crystal orientation modification, and formic acid vapour treatment have been discussed in detail and the advantages and disadvantages of each process have been mentioned. The easiest and cost effective processes are surface pre-treatment with different chemicals but technique is not suitable for the 3-D integration because it requires the wafer to be aligned in bond aligner before bonding and there is a chance of re-oxidation during transferring the samples to wafer bonder from bond aligner. In-situ treatment using forming gas will give better result because reoxidation can be avoided, but this requires a costly dedicated apparatus and process has to be optimized for reducing the effect of forming gas on surface finish. Current trends for low temperature Cu-Cu bonding is by using passivation either metal passivation or SAM to protect Cu wafer from oxidation before bonding and achieving the good bond strength at low temperature (<180°C). There is no chance of re-oxidation in the case of metal passivation, but still metal passivation layer thickness has to be optimized. With consideration of above facts, this paper will give an idea to researchers to choose the suitable technique for achieving the low-temperature Cu-Cu bonding process using various techniques reported in this paper which could have a great influence on heterogeneous integration of Micro-systems.

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