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Anti-oxidant copper layer by remote mode N₂ plasma for low temperature copper–copper bonding

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An anti-oxidant Cu layer was achieved by remote mode N₂ plasma. Remote mode plasma treatment offers the advantages of having no defect formation, such as pinholes, by energetic ions. In this study, an activated Cu surface by Ar plasma chemically reacted with N free radicals to evenly form Cu nitride passivation over the entire Cu surface. According to chemical state analysis using XPS, Cu oxidation was effectively prevented in air, and the thickness of the Cu nitride passivation was within 3 nm. Based on statistical analysis using the DOE technique with N₂ plasma variables, namely, RF power, working pressure, and plasma treatment time, we experimentally demonstrated that a lower RF power is the most effective for forming uniform Cu nitride passivation because of a lower plasma density. When the N₂ plasma density reached approximately 10⁹ cm⁻³ in which the remote mode was generated, high energy electrons in the plasma were significantly reduced and the amount of oxygen detected on the Cu surface was minimized. Finally, low temperature (300 °C) Cu–Cu bonding was performed with a pair of the anti-oxidant Cu layers formed by the remote mode N₂ plasma. Cu atomic diffusion with new grains was observed across the bonded interface indicating significantly improved bonding quality over bare Cu–Cu bonding.

In advanced packaging such as 3D packaging that vertically stacks the manufactured chips and heterogeneous packaging that places various chips in a limited area, Cu–Cu bonding as electrical connections between the chips is a key process for the high performance and reliability of the entire system^{1–10}. In order to protect a device from thermal damage in device stacking, a low temperature (≤ 300 °C) Cu–Cu bonding process is essential. However, low temperature Cu–Cu bonding is interrupted by the native oxide film such as Cu₂O which blocks Cu atomic diffusion at the Cu–Cu bonding interface^{11,12}. Thus, Cu–Cu bonding generally requires a bonding temperature higher than 400 °C to break Cu oxide layer.

Many Cu–Cu bonding studies have been reported on lowering the bonding temperature. One such approach is removing the native oxide film that has already formed on a Cu surface. This approach includes a surface activated bonding (SAB) method^{13,14} that breaks the Cu oxide layer and activates the Cu surface using collision from a high energy Ar beam and a wet treatment method^{15,16} that chemically removes the Cu oxide layer using various acids, such as sulfuric acid (H₂SO₄), acetic acid (CH₃COOH), and citric acid (C₆H₈O₇). Alternatively, there is a way to prevent Cu oxidation from the beginning. Temporary passivation using a self-assembled monolayer (SAM) of alkane-thiol^{17,18} and metal passivation using Ti, Pd, Ag, or Au^{19,20} allow the Cu surface to remain pristine.

For high-volume manufacturing (HVM), Cu–Sn alloys have been applied to eutectic bonding thanks to its low melting point with a reasonable electrical conductivity^{21,22}. Although Sn is used as a cap on the top of a Cu pillar bump, it is not suitable for a fine pitch (≤ 10 μm) process due to the reflow characteristics. In addition, the formation of intermetallic compounds (IMC) and the growth of Kirkendall void at the bonding interface degrade mechanical and electrical properties of the Cu/Sn/Cu interconnects. The Direct Bond Interconnect (DBI) technology^{23,24} is currently used in low temperature hybrid bonding applications, for example, in CMOS image sensors (CIS). That technology forms oxide–oxide bonding, and then a uniform shallow Cu recess is annealed at a low temperature (150–300 °C) to establish a Cu–Cu connection using the difference in the coefficient of thermal

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expansion between the oxide and Cu. However, that method requires a highly accurate chemical mechanical polishing (CMP) process control, and it is hard to apply it to ultra-fine pitch for the next generation.

With this background, we propose a passivation process using a Cu nitride layer in a low temperature Cu–Cu bonding method. This technique has numerous advantages compared to the other methods introduced above. First, our passivation process is CMOS compatible because it is a dry process that uses plasma treatment. It is also inexpensive and simple because the process is performed with a conventional DC sputter used for the Cu thin film deposition by common gases such as argon and nitrogen. Moreover, Cu nitride passivation protects the Cu surface from oxidation in the atmosphere, but it is easily decomposed at a low bonding temperature because of its thermodynamic instability. This characteristic helps to form a homogeneous bonded layer in a low temperature Cu–Cu bonding process.

In this study, the Cu nitride passivation was formed using a two-step Ar/N₂ plasma process. Because the Cu nitride passivation can be damaged from the accompanying sputtering effect by Ar ion bombardment, the Ar + N₂ mixed gas is unfavorable to the formation of uniform and thin copper nitride passivation in manufacturing. Therefore, we propose the two-step Ar/N₂ plasma process: Ar plasma pre-treatment was performed first on a Cu surface to remove any contaminants and to activate Cu atoms before the N₂ plasma treatment. Then, the N free radicals generated by the dissociation of N₂ molecules in the N₂ plasma chemically react with the activated Cu atoms at the Cu surface to form Cu nitride passivation. We report the effect of our two-step Ar/N₂ plasma process on the Cu surface, the mechanism of the formation of Cu nitride passivation, and the bonding quality of low temperature Cu–Cu bonding using an anti-oxidant Cu layer.

Methods

Sample fabrication flow and DOE setup. An 8-inch Si wafer with a 700 nm thick SiO₂ layer was diced into a chip size of 1 cm². Each piece of diced Si chip specimen was fixed by Kapton tape on an 8-inch dummy Si wafer. Using DC magnetron sputtering, a 50 nm thick Ti adhesion layer and 1 μm thick Cu thin film were deposited on the diced Si chip specimens under 5 mTorr working pressure and 2500 W DC power. After the Cu deposition, two-step Ar/N₂ plasma treatment was performed in the same sputter chamber with maintained vacuum conditions. For the plasma treatment, RF power of 13.56 MHz was applied to a table chuck where the specimen was located, and it became a cathode. In this study, we focused on the effect of N₂ plasma variables on the formation of Cu nitride passivation. Thus, we fixed the variables of the Ar plasma process while we evaluated the N₂ plasma process under the statistically designed conditions. In the design of experiment (DOE) method, central composite design (CCD) was used for a response surface methodology (RSM) which is an efficient DOE method that estimates the regression coefficient of a quadratic polynomial model with only a few experiments^{25,26}. A total of 20 experiments for the N₂ plasma process consisted of 8 points from the 3-factor (RF power, working pressure, and treatment time) 2-level (low or high) full factorial design experiments, 6 axial points, and 6 center points. The detailed two-step Ar/N₂ plasma process conditions are listed in Table 1 and a study on the Ar plasma process using the full factorial DOE method was reported in previous paper²⁷.

For the Cu–Cu bonding process, the above deposition procedure and two-step Ar/N₂ plasma process were carried out on an 8-inch Si wafer. A pair of Cu blanket wafers were bonded at 300 °C under 700 kPa for 1 h using a thermo-compression bonding method in the SB 8e wafer bonder of SUSS Microtech.

The chemical state of Cu surface and Cu–Cu bonding interface analysis methods. The chemical state of the two-step Ar/N₂ plasma treated Cu surface was analyzed by X-ray photoelectron spectroscopy (XPS). The peak profiles for three elements, Cu, O, and N, were measured using a Thermo Scientific K-Alpha⁺ XPS system with a micro-focused monochromatic Al Kα (hν = 1486.6 eV) X-ray source of 72 W at 12 kV.

The bonding quality of the bonded wafer was evaluated using scanning acoustic tomography (SAT) of Hitachi FineSAT III with a 140 MHz probe. For a detailed analysis of the bonding interface, the bonded wafer was diced into 1 cm² specimens and the diced plane was polished by Ar ion beam milling using JEOL Ltd. IB-19510CP. Then the polished clear cross section was analyzed by field emission scanning electron microscope (FE-SEM) using FEI Company Apreo S HiVac with 20,000× magnifications.

Results and discussion

The chemical state analysis of the two-step Ar/N₂ plasma treated Cu surface by XPS. Figures 1a–c compare the XPS profiles of the two-step Ar/N₂ plasma treated Cu and non-plasma treated Cu, and Table 2 shows the reference binding energy of several Cu compounds^{28–31}. After the plasma treatment, the main peak of the Cu2p_{3/2} profile in Fig. 1a shifted towards a higher binding energy (from 932.48 eV to 932.58 eV) indicating that a pure metallic Cu (Cu⁰) combined with other elements and new substances were created, namely, Cu nitride (Cu¹⁺) or cupric oxide (Cu²⁺). On the other hand, the main peak of the non-plasma treated Cu shifted towards a lower binding energy (from 932.48 eV to 932.28 eV) than pure Cu due to the formation of cuprous oxide (Cu¹⁺), which indicated oxidation in air. In addition, a noticeable peak at 530.38 eV of the O1s profile in Fig. 1b disappeared while a new peak at 397.38 eV of the N1s profile in Fig. 1c appeared. Therefore, the chemical states of the new peak of the N1s profile and the removed peak of O1s profile are considered as a Cu nitride layer and native oxide grown on Cu, respectively. The stoichiometry of each compound was estimated to be close to Cu₄N and Cu₂O by atomic concentration calculation (not shown here). In order to analyze the thickness of the Cu₄N, XPS depth profiling was performed for 50 s at intervals of 10 s with an etch rate of 0.1 nm/sec. The Cu2p_{3/2} main peaks of the two-step Ar/N₂ plasma treated Cu shown in Fig. 1d and the non-plasma treated Cu shown in Fig. 1g appeared at a binding energy value for pure Cu after 30 s. The Cu₄N peak of the N1s profiles shown in Fig. 1f clearly appeared until 30 s of depth profiling, which indicated that the thickness of the Cu nitride was approximately 3 nm. In contrast, there is no peak in Fig. 1i after 10 s because the non-plasma treated

Coded factor	Actual factor	Coded level and actual level				
		$-\alpha$	-1	0	+1	$+\alpha$
A	RF power	25.68	70	135	200	244.32
B	Pressure	3.48	4.5	6	7.5	8.52
C	Time	31.82	100	200	300	368.18
Ar plasma treatment conditions						
Specimen	Flow rate (sccm)	RF power (W)	Pressure (mTorr)	Time (s)		
Step 1 (fixed)						
All	150	100	7.5	30		
N ₂ plasma treatment conditions						
Specimen	Flow rate (sccm)	RF power (W)	Pressure (mTorr)	Time (s)		
Step 2						
1	45	70	4.5	100		
2		200	4.5	100		
3		70	7.5	100		
4		200	7.5	100		
5		70	4.5	300		
6		200	4.5	300		
7		70	7.5	300		
8		200	7.5	300		
9		26	6.0	200		
10		244	6.0	200		
11		135	3.5	200		
12		135	8.5	200		
13		135	6.0	32		
14		135	6.0	368		
15		135	6.0	200		
16		135	6.0	200		
17		135	6.0	200		
18		135	6.0	200		
19		135	6.0	200		
20		135	6.0	200		

Table 1. Independent factors and levels (coded and actual) for CCD design (top), fixed Ar plasma treatment conditions (middle), N₂ plasma treatment conditions designed by CCD (bottom).

Cu has only chemisorbed nitrogen atoms ($N_{\text{chemisorbed}}$) on the Cu surface. The Cu₂O peak of the O1s profile in non-plasma treated Cu shown in Fig. 1h was observed up to 30 s, which means that about 3 nm of native Cu oxide was formed without the plasma treatment. A peak of the O1s profile in the two-step Ar/N₂ plasma treated Cu shown in Fig. 1e was observed until 10 s, however, it is considered as the peak due to chemisorbed oxygen atoms generated from a hydroxyl group (–OH) during depth profiling. Using the deconvolution technique, the binding energy, Cu–O peak area, and Cu–N peak area of the Cu2p_{3/2} profile and the Cu–N peak area of the N1s profile for all the specimens are plotted in Fig. 2. In the Cu2p_{3/2} profiles, all plasma treated Cu specimens have a Cu–N (Cu₄N) peak area that is almost 10 times greater than its Cu–O (CuO) peak area. Moreover, Note that –OH peak area might be included in Cu–O peak area during the deconvolution analysis because the CuO peak is adjacent to the Cu(OH)₂ peak within the narrow area of the Cu2p_{3/2} profile. Therefore, we considered the small area of Cu–O peak of the two-step Ar/N₂ plasma treated Cu specimens to be negligible, and the surface of specimen 9 in particular to be an anti-oxidant Cu layer. In sharp contrast, the non-plasma treated Cu specimen had a significant amount of Cu–O (CuO + Cu₂O) peak area. This was in agreement with the binding energy shift of the Cu2p_{3/2} main peak. These results prove that Cu oxide was effectively removed after the two-step Ar/N₂ plasma treatment.

Effect of the N₂ plasma variables on the formation of Cu nitride passivation. To understand the effect of the N₂ plasma variables on the formation of Cu nitride passivation, the correlation between the N₂ plasma variables and the Cu₄N peak area (also the CuO peak area just for comparison) of the Cu2p_{3/2} was statistically analyzed at 95% confidence ($\alpha = 0.05$) using a Minitab program. The Pareto chart of the standardized effects and main effects plot for Cu₄N and CuO are shown in Fig. 3a–d. Among the three variables (A: RF power, B: working pressure, and C: treatment time), the RF power (AA) is the most dominant factor for the Cu₄N formation, and the working pressure and treatment time do not have much effect. AA is a quadratic term of the variable A, meaning that the variable and response (XPS peak area) have a nonlinear correlation. From the main effects plot, the lower RF power leads to more Cu₄N formation, but meanwhile, the analysis results for the

Figure 1. XPS analysis of $\text{Cu}2p_{3/2}$, $\text{O}1s$, and $\text{N}1s$: (a–c) surface profiles of two-step Ar/N_2 plasma treated Cu and non-plasma treated Cu, (d–f) depth profiles of two-step Ar/N_2 plasma treated Cu and (g–i) depth profiles of non-plasma treated Cu for 50 s.

Linked to	$\text{Cu}2p_{3/2}$ (eV)	$\text{O}1s$ (eV)	$\text{N}1s$ (eV)
Cu	932.0–932.5	–	–
Cu_2O	932.2–932.8	529.9–530.6	–
CuO	933.6–934.4	529.4–529.8	–
$-\text{OH}$	935.0–935.3	~531.2	–
$\text{N}_{\text{chemisorbed}}$	–	–	398.3–400.0
Cu_4N	932.2–932.7	–	~397.4

Table 2. Reference XPS binding energies of the Cu compounds^{28–31}.

CuO are the opposite because CuO production is prevented by Cu_4N . Additional analysis results for the Cu_4N peak area of the $\text{N}1s$ shown in Fig. 3e and the CuO peak area of the $\text{O}1s$ shown in Fig. 3f coincide with those for $\text{Cu}2p_{3/2}$ shown in Fig. 3c,d. The effect of RF power in N_2 plasma treatment is explained in detail below.

Effect of the RF power on the N_2 plasma density. Depending on the applied RF power (P_{RF}), electrons inside the plasma collide with molecules or atoms to transfer energy or dissipate into the wall. The power absorbed by electrons (P_{abs}) is balanced with the power consumed by generation of electrons and ions through

Figure 2. XPS peak analysis by a deconvolution technique.

various collisions at a steady state (P_{loss}). Therefore, if we ignore the power loss that occurred in the RF matching box, we can assume that $P_{\text{RF}} = P_{\text{abs}} = P_{\text{loss}}$, and the total power loss is as follows^{32,33}.

$$P_{\text{loss}} = n_s u_B A e \varepsilon_T \quad (1)$$

where n_s , u_B , A , and $e \varepsilon_T$ represent the electron density at the sheath boundary, Bohm velocity (the sound speed for cold ions), interior area of the plasma chamber, and total loss energy required to generate an electron-ion pair, respectively. The n_s has a relationship with the plasma density n_0 as $n_s = h(\lambda_i) n_0$ and where λ_i is an ion mean free path, h denotes the plasma density ratio to the radial (h_R) and axial (h_L) directions in the plasma chamber when the radius of the plasma chamber is R and the height is L . Equation (1) can be expressed as $P_{\text{loss}} = P_{\text{RF}} = h(\lambda_i) n_0 u_B A e \varepsilon_T$, where $h(\lambda_i) A = A_{\text{eff}} = 2\pi R^2 h_L + 2\pi R L h_R$. Finally, the equation for the plasma density becomes^{32,34}

$$n_0 = \frac{P_{\text{RF}}}{u_B e \varepsilon_T A_{\text{eff}}} \quad (2)$$

The three terms of the denominator are a function of the electron temperature and are negligible for the plasma density within the designed experimental range in this research. On the other hand, the plasma density significantly increases in proportion to the RF power (26–244 W), and the calculated plasma density as a function of the RF power is plotted in Fig. 4. The blue circle marks show the major values of RF power in the CCD (26, 70, 135, 200, and 244 W) in this DOE setup. When the plasma density decreases to $\sim 10^9$ with a RF power reduction, the chemical reaction rate decreases due to the low ionization rate of the N_2 plasma. Thus, a thick sheath is formed and the plasma becomes a remote mode where very few charged species reach into the substrate³⁵. In this remote mode, many more N free radicals are generated than N_2^+ and N^+ ions by the high ratio of electrons with low energy in the plasma. Consequently, chemical reactions for the formation of Cu nitride passivation by radicals dominate on the Cu surface rather than ion bombardment. As the plasma density increases, the plasma is converted to the direct mode and reactive ion etching (RIE) mode. These modes disturb the formation of the Cu nitride passivation because the sputtering effect caused by energetic ions accompanies it. Table 3 compares the plasma properties according to each plasma mode.

Electron energy distribution in the remote mode N_2 plasma. The ionization, dissociation, and excitation reaction of neutral particles in the plasma depend on the kinetic energy of the electrons, and the kinetic energy of the electrons is proportional to the electron temperature. The electron temperature T_e can be calculated simultaneously by Eq. (3) for the power balance equation and particle balance equation^{32,36}.

$$\frac{K_{iz}(T_e)}{u_B(T_e)} = \frac{1}{n_g d_{\text{eff}}} = \frac{1}{n_g} \frac{A_{\text{eff}}}{V} \quad (3)$$

where K_{iz} is the ionization rate coefficient, gas density $n_g = (3.3 \times 10^{19})p$ and p is the working pressure. Since the plasma chamber size is fixed, we can ignore the terms A_{eff} and V in Eq. (3). That is, the electron temperature is only affected by the working pressure (3.5 to 8.5 mTorr), and the electron temperature exponentially decreases as the working pressure increases. This is because when the working pressure increases at a constant plasma condition, the amounts of ions and electrons increase, and the heat energy absorbed per electron decreases.

Figure 3. Analysis of the response surface design at 95% confidence level using a Minitab program (a) the Pareto chart of the standardized effects for the Cu_4N peak of the $\text{Cu}_2\text{p}_{3/2}$, and the place where the term crosses the reference line is statistically significant, (b) the Pareto chart of the standardized effects for CuO peak of the $\text{Cu}_2\text{p}_{3/2}$, and (c-f) the main effects plot calculated by the response for Cu_4N and CuO in the $\text{Cu}_2\text{p}_{3/2}$, $\text{O}1\text{s}$, and $\text{N}1\text{s}$.

As the electron temperature along with the plasma density greatly affects the electron energy distribution function (EEDF), we can infer the chemical reactions occurring in the plasma through the EEDF. If we assume that the EEDF follows the Maxwell distribution, the equation can be written as^{32,37,38}

$$f(\varepsilon) = \frac{2n_e}{\sqrt{\pi}} \frac{1}{(T_e)^{3/2}} \sqrt{\varepsilon} e^{-\varepsilon/T_e} \quad (4)$$

where ε is the electron energy and n_e is the electron density, which is considered to be equal to the plasma density. Figure 5 shows the constructed EEDF and it demonstrates the electron energy distributions with the electron temperature and the plasma mode. The lower electron temperature, the higher distribution of electrons with lower energy, and the reactive species in the plasma significantly decrease in the remote mode with a low plasma density.

Figure 4. Plasma density and mode depending on the RF power.

Plasma mode	Remote	Direct	RIE
Density (cm ⁻³)	≈ 10 ⁹	~ 10 ¹⁰	10 ¹⁰ –10 ¹¹
Sputtering effect	Almost-free	Small	Large
Application	Surface treatment (by radical)	PECVD plasma etching	Reactive ion etching (anisotropic)
Schematic diagram

Table 3. Plasma properties of each plasma mode.

Figure 5. Electron energy distribution function (EEDF) with electron temperature and the plasma mode.

Element	Reactions in the plasma	Electron energy (eV)
Ar	$\text{Ar (g)} + \text{e}^- \rightarrow \text{Ar}^+ \text{ (g)} + 2\text{e}^-$	15.8
N_2	$\text{N}_2 \text{ (g)} + \text{e}^- \rightarrow 2 \text{N (g)} + \text{e}^-$	9.8
	$\text{N}_2 \text{ (g)} + \text{e}^- \rightarrow \text{N}_2^+ \text{ (g)} + 2\text{e}^- \text{ (g)}$	15.3
	$\text{N}_2 \text{ (g)} + \text{e}^- \rightarrow \text{N}^+ \text{ (g)} + \text{N (g)} + 2\text{e}^-$	24.3
Cu	$\text{Ar}^+ \text{ (g)} + \text{Cu (s)} \rightarrow \text{Ar}^+ \text{ (g)} + \text{Cu}^+ \text{ (g)} + \text{e}^-$	11.24

Table 4. Main reactions for each element in the plasma and required electron energy^{36,39}.

If the kinetic energy of electrons in the plasma is insufficient, excitation or dissociation occurs more than ionization. In our experiments, most electrons in the plasma had low electron energy ($T_e < 2.4$ eV) because a significant amount of energy was consumed as collisional energy for ionization or dissociation of N_2 molecules. Therefore, the unstable state of the N free radicals generated by low-energy electron collision reached the Cu surface, and metastable Cu nitride passivation in the form of Cu_4N was produced rather than Cu_3N . Table 4 lists the energy required for dissociation and ionization of Ar, N_2 , and Cu^{36,39}.

The mechanism of the Cu_4N formation and Cu–Cu bonding. To study the mechanism of the Cu_4N formation, we calculated the standard enthalpy of formation. The standard enthalpy of formation of Cu_4N has not been reported yet, so we derived it according to the Born-Haber cycle using the enthalpy of Cu_2O and Cu_3N from the literature^{40,41}. The standard enthalpies of formation for several Cu compounds (Cu_2O , Cu_3N , and Cu_4N) are calculated in Fig. 6a–c. The equation for the standard enthalpy of formation is expressed as

$$\Delta H_{\text{atomization}} + \Delta H_{\text{ionization energy}} + \Delta H_{\text{electron affinity}} + \Delta H_{\text{lattice formation}} = \Delta H_{\text{formation}} \quad (5)$$

As demonstrated in Fig. 6b, the mechanism of Cu_3N formation is explained as follows. In order for solid Cu to be ionized, first the metallic bond must be broken and then it becomes a Cu atom ($\text{Cu (s)} \rightarrow \text{Cu (g)}$), and the atomization energy of Cu is 3.51 eV. The strong triple bond of the N_2 molecule is also broken to produce a N free radical ($\text{N}_2 \text{ (g)} \rightarrow 2 \text{N (g)}$), which requires 9.8 eV of dissociation energy. With the first ionization energy of 7.73 eV, the Cu atom removes a valence electron and then becomes a Cu^+ ion. At the same time, the neighboring N free radical that reached the Cu surface obtained three electrons, one per Cu and then became a N^{3-} ion ($\text{N (g)} \rightarrow \text{N}^{3-} \text{ (g)}$). Finally, three positive Cu ions and a negative N ion formed Cu_3N through ion bonding with an exothermic reaction, and the standard enthalpy of formation of Cu_3N reported by M. Akira is 0.77 eV⁴¹. Here, the total energy of the entire chemical reaction is conserved, so the lattice formation enthalpy is -59.80 eV.

The mechanism of Cu_4N formation can be explained in the same way as shown in Fig. 6c. Cu_4N has one more Cu atom than Cu_3N , but the lattice formation enthalpy of Cu_4N is assumed to be the same as Cu_3N because the Cu atom is interstitially doped into the empty space of Cu_3N , which has a cubic anti- ReO_3 crystal structure⁴². Therefore, the standard enthalpy of formation of Cu_4N is 13.23 eV, which is quite high compared to Cu_2O (-1.75 eV) as shown in Fig. 6a. Cu_2O has a negative enthalpy, so it is chemically stable and hard to be decomposed. It makes Cu–Cu bonding difficult at low temperature because the Cu_2O prevents the diffusion of Cu at the bonding interface. However, when the Cu_4N is in a metastable state, it can be decomposed at a lower temperature than the bonding temperature, which results in pure Cu–Cu bonding. Hence, this mechanism provides spontaneous Cu–Cu bonding at low temperature. The entire bonding process and mechanism, including the formation and decomposition of Cu nitride passivation, are shown in Fig. 7.

The evaluation of the bonded interface of anti-oxidant Cu–Cu bonding. A pair of Cu wafers of two types were bonded at 300 °C under 700 kPa for 1 h using a thermo-compression bonding method. Figure 8 shows the SAT and FE-SEM images for both the bare Cu–Cu bonding using non-plasma treated Cu and the anti-oxidant Cu–Cu bonding using remote mode N_2 plasma treated Cu in the two-step Ar/ N_2 plasma process. In the SAT analysis, note that any unbonded voids appear as white color due to the reflection of the ultrasonic signal. As shown in Fig. 8 (left), bare Cu–Cu bonding has an extremely poor bonded interface, which is due to Cu surface oxidation; moreover, the cross-sectional image of the bonded interface in the FE-SEM image clearly shows an unbonded interface. On the other hand, anti-oxidant Cu–Cu bonding demonstrates an improved bonding quality in most of the wafer except for the central region. This unbonded area appears to be caused by trapped N_2 gas when the Cu nitride passivation on the entire wafer is thermally decomposed during the bonding process. In addition, there was Cu atomic diffusion with new grains across the bonded interface. Considering that this is whole Cu blanket wafer bonding without a CMP process, it demonstrates a significant improvement and a high potential for low temperature Cu–Cu bonding.

Figure 6. The standard enthalpy of formation according to the Born-Haber cycle (1 eV = 96.485 kJ/mol) (a) Cu₂O, (b) Cu₃N, and (c) Cu₄N.

Conclusion

A low temperature Cu–Cu bonding process is essential in advanced 3D device stacking technologies to protect the devices from thermal damage, and the key point of Cu–Cu bonding is preventing oxidation on a Cu surface especially for die-to-wafer stacking. In this study, we protected the Cu surface from oxidation by the formation of Cu nitride passivation using a two-step Ar/N₂ plasma treatment. After the Cu surface activation by Ar plasma pre-treatment, N free radicals in the N₂ plasma treatment reacted with the Cu surface to form Cu nitride passivation. According to a chemical state analysis of the two-step Ar/N₂ plasma treated Cu surface by XPS and a calculation of the standard enthalpy of formation, the Cu nitride layer effectively prevented the formation of native Cu oxide and it promotes spontaneous Cu–Cu bonding.

We statistically analyzed the effect of N₂ plasma variables on the formation of Cu nitride passivation by the RSM using a CCD in DOE methodology. Among the N₂ plasma variables, RF power was the most effective factor for the formation of Cu nitride passivation, and a lower RF power generated the remote mode N₂ plasma. An anti-oxidant Cu layer was obtained in the remote mode N₂ plasma with low electron temperature and low plasma density. A pair of anti-oxidant Cu wafers were bonded at 300 °C, and the bonding quality was significantly improved over bare Cu–Cu bonding.

In the future, we will optimize the N₂ plasma treatment conditions to provide improved Cu–Cu bonding quality at a lower temperature and perform electrical and mechanical evaluations.

1. Cu deposition

Cu + few contaminants

2. Ar plasma treatment **3. N₂ plasma treatment** **4. Exposed to air** **5. Ramping up the temperature** **6. Cu-Cu bonding**

Figure 7. Low temperature Cu–Cu bonding mechanism using an anti-oxidant Cu layer by remote mode N₂ plasma in the two-step Ar/N₂ plasma process, including the formation and decomposition of Cu nitride passivation.

Figure 8. SAT and FE-SEM evaluation of the Cu–Cu interface bonded at 300 °C: (left) bonding with non-plasma treated Cu wafers and (right) bonding with two-step plasma treated Cu wafers.

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Author contributions

All authors discussed the results. H.P. contributed to design of plasma treatment conditions, analyzed the effects of plasma variables, and XPS, SAT data analysis. H.S. contributed specimen fabrication and XPS, FE-SEM data analysis. S.E.K. devised research ideas and advised on experimental data.

Competing interests

The authors declare no competing interests.

Additional information

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