Development of CMOS-Compatible Low Temperature Cu Bonding Optimized by the Response Surface Methodology

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***Abstract*—As an interconnect scaling in planar (2D) chips face a technical bottleneck, the vertically stacked structure called 3D integrated circuit (IC) packaging becomes a major packaging technology for the next generation heterogeneous integration. 3D IC packaging technology provides reduced interconnect lengths between the chips and improves electrical signal and power delivery problems. Among three core unit processes in 3D packaging, a wafer bonding process is still an immature process for mass production compared to through Si via formation and Si thinning. Most bonding materials used in stacked ICs so far are solder materials or Cu pillars with Sn cap, however with the demand of fine pitch less than 10um in a bonding layer, Cu bonding is of great interest in 3D IC heterogeneous packaging. Despite the excellent electrical and mechanical properties and fine pitch patternability, Cu bonding process has several challenges to be resolved, such as easy oxidation, high bonding temperature, extremely low dishing planarization and so on. In this study, the two-step plasma treatment method using Ar and N_2 was applied on the copper surface to achieve low temperature Cu bonding. N_2 plasma process of two-step plasma treatment was optimized by RSM (response surface methodology) based on CCD (central composite design) in DOE (design of experiment) system. With the optimized plasma treatment, the Cu bonding quality has been significantly improved compared to Cu bonding without any surface treatment at 300°C. Also, it has been demonstrated that the copper nitride passivation layer prevents further oxidation up to 1 week in air.**

Keywords-Cu bonding; Low temperature bonding; Copper nitride passivation; Ar-N_2 plasma treatment; Design of Experiment; Response Surface Methodology

I. INTRODUCTION

The increase of semiconductor integration with small feature has reached a level that could not be fabricated by conventional patterning method. To overcome these technical bottlenecks of an interconnect scaling, 3D integrated circuit (IC) packaging has been focused as an alternative [1-4]. Unlike 2D planar ICs, 3D IC packaging technology could significantly reduce signal delay, power consumption, and form factor without a device scaling-down technology. Also, it offers heterogeneous integration and high bandwidth [5-7]. To fabricate a 3D IC packaging system, there are three core unit processes that are TSV (through Si via) formation, Si wafer grinding, and chip-to-wafer or wafer-to-wafer bonding. Generally, the TSV formation consists of etching and filling processes. The tens of thousands of via holes with high aspect ratio formed by deep Si etching and then conformal filling without voids [8-9]. For Si thinning, it is important to manage the warpage and handling of the thinned Si wafer since a thinned Si wafer tends to break easily or even to roll up [10]. Also, the control of total thickness variation (TTV) is very critical for Si thickness less than 30 μm. A chip-to-wafer bonding is well developed so far, and a wafer-to-wafer bonding is still considered as an immature technology for mass production compared to TSV formation and Si thinning process. In terms of bonding materials, solder materials or Cu pillars with Sn cap have been used in stacked ICs, however, an intermetallic compound (IMC) at the bonding interfaces causes electrical and mechanical reliability problems. Also, these solder materials cannot meet a strong demand of fine pitch less than 10 μm in a bonding layer due to a reflow property. On the other hand, Cu is an outstanding bonding material in 3D IC heterogeneous packaging because of its excellent scalability, and electrical conductivity. Despite these advantages, Cu has several challenges such as easy oxidation, high bonding temperature, low surface roughness, and extremely low dishing planarization. For these reasons, many studies on low temperature Cu bonding have been reported over the last few decades.

C. S. Tan reported Cu-Cu die-to-die surface activated bonding (SAB) using two different types of plasma namely Ar and Ar+N_2 plasma for surface activation [11]. T. Suga also proposed SAB to clean and activate the surface by colliding Cu surface with a high energy Ar beam added Si atoms [12]. C. Chen achieved Cu-Cu bonding in no-vacuum ambient using highly (111) oriented and nanotwinned Cu structure [13]. A. K. Panigrahy induces Cu atom diffusion at

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the anti-oxidation and bonding interface using Ti passivation [14]. D. F. Lim applied the temporary passivation using self-assembled monolayer (SAM) of alkane-thiol on Cu surface for low temperature bonding [15].

In this report, the two-step plasma treatment using Ar and N_2, which is an excellent CMOS-compatible process, is introduced for low temperature Cu bonding. The first step is Ar plasma process to clean and activate Cu surface, and the second step is N_2 plasma process to passivate Cu surface from oxidation. Our two-step plasma treatment on Cu surface was optimized by the response surface methodology in the design of experiment (DOE), and a bonded interface was analyzed by SAT (scanning acoustic tomography) and the sustained effect of the copper nitride passivation layer over time was evaluated.

II. Experimental

The schematic diagram of Cu bonding experiment with the two-step plasma is demonstrated in Fig. 1. 8-inch notch type Si wafer was prepared as a substrate and a uniform oxide film (SiO_2) with a thickness of 700 nm was grown by a thermal oxidation process. Then 50nm-thick Ti and 1μm-thick Cu thin films were deposited by a conventional DC sputtering sequentially. The Cu specimen (Cu/Ti/SiO_2/Si) is kept on a wafer chuck in a DC sputter chamber with a high vacuum environment until the end of plasma treatment. In the first plasma step, Ar ions bombard Cu surface to remove copper oxides and any contaminants producing Cu dangling bonds. In the second step, Cu nitride passivation is formed on the activated Cu surface by nitrogen radical inside the N_2 plasma. The two-step plasma treatment is more effective process compared to Ar and N_2 mixed plasma treatment. Because Ar and N_2 mixed plasma can form and decompose Cu nitride simultaneously, making it difficult to offer uniform Cu nitride over an entire Cu surface.

In this two-step plasma treatment study, the conditions of Ar plasma were fixed, and the N_2 plasma conditions were varied by the response surface methodology (RSM) based on a central composite design (CCD) in design of experiment (DOE) method. The RSM in DOE efficiently estimates the square terms of quadratic models for process optimization and is useful for orthogonal blocking [16]. The total test specimen were 20 points by the RSM, which consists of 8 points from a 3-factor/2-level full factorial design experiment, 6 axial points, and 6 repeated center points, as shown in Fig. 2 and Table I. The detailed experimental conditions are listed in our previous report [17]. The chemical analysis of Cu surface after the two-step plasma treatment for the optimized Cu bonding was done by X-ray photoelectron spectroscopy (XPS). Cu bonding was performed at 300°C under 700 kPa for 1hour using a thermo-compression bonding method. A bonded interface of the optimized Cu bonding specimen was evaluated using scanning acoustic tomography (SAT). In addition, the sustained effect of copper nitride passivation was studied over time for 0-hour, 6-hour, 1-day, 3-day, and 1-week in air. Both oxygen (O1s) and nitrogen (N1s) chemical states of these samples were evaluated using XPS analysis.

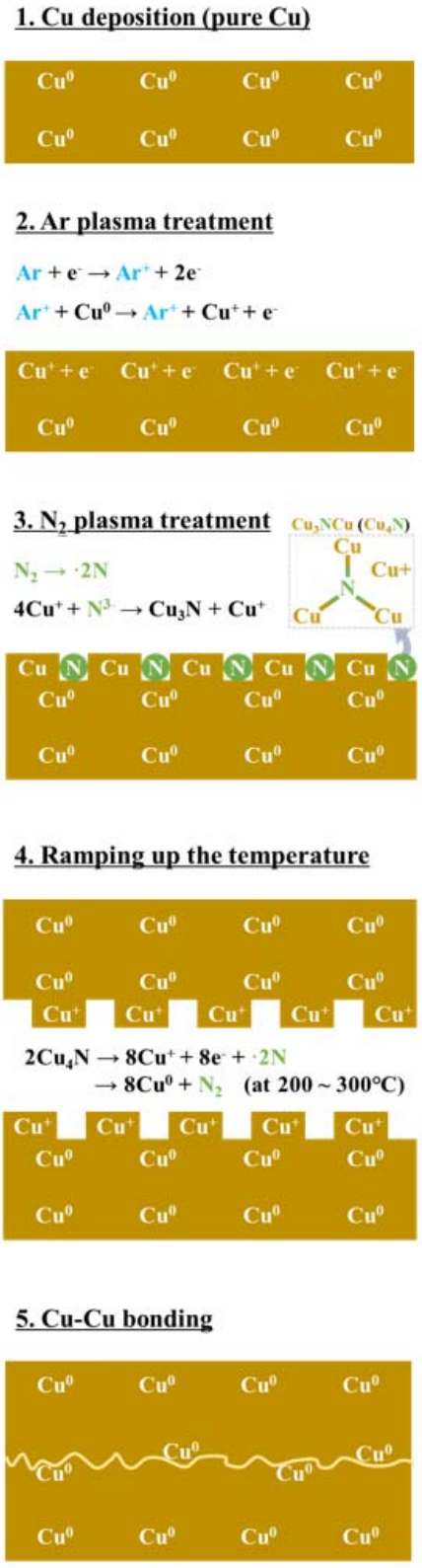

Figure 1. Cu bonding process using two-step plasma treatment

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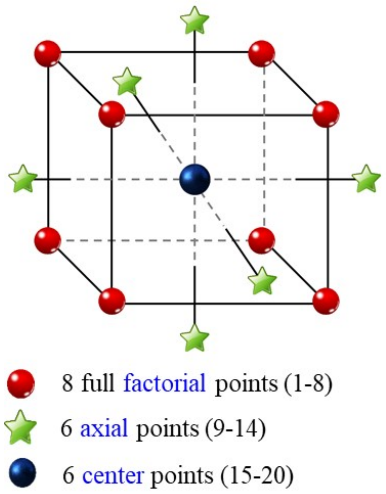

Figure 2. Cubic model for RSM design based on CCD method

TABLE I. EXPERIMENTAL RANGE OF VARIABLES AND CODED VALUES OF 3 VARIABLES IN RSM

Factor	Unit	Level				
		-α	*-1*	*0*	*+1*	*+α*
RF power	W	25.68	70	135	200	244.32
Pressure	mTorr	3.48	4.5	6	7.5	8.52
Time	s	31.82	100	200	300	368.18

III. RESULTS AND DISCUSSION

A. Chemical analysis of Cu surface by XPS

The chemical composition and bonding state of Cu surface after the two-step plasma treatment was studied by XPS using K-alpha XPS system that uses a monochromatic Al Kα source (hν = 1486.6 eV). Fig. 3 shows $Cu2p_{3/2}$, O1s, and N1s profiles corresponding to the light emission spectra of Cu, O, and N elements before (labelled as N) and after the two-step plasma treatment (labelled as 1~20). After the two-step plasma treatment, the binding energy of $Cu2p_{3/2}$ main peak moved to a higher binding energy by 0.1~0.2 eV. The increase in binding energy and occurrence of shoulder peak mean that a pure metallic Cu (Cu^0) is combined with other elements to change into Cuprous (Cu^{1+}) or Cupric (Cu^{2+}) ion. The cause of this shift in $Cu2p_{3/2}$ binding energy can be found in the O1s and N1s profiles too. After the two-step plasma treatment, the 530.21 eV peak in the O1s profile was removed, whereas a new peak of 397.28 eV was found in the N1s profile in all specimens. This correlation indicates that the two-step plasma treatment effectively removed copper oxides and formed copper nitride passivation. XPS peak area was measured by a deconvolution technique for the stoichiometry calculation and optimization of N_2 plasma process. Three peaks (Cu_4N, CuO, and $Cu(OH)_2$) were used for the $Cu2p_{3/2}$ peak deconvolution and two peaks (Cu_4N and $N_{chemisorbed}$) were used for the N1s peak deconvolution. In case of the O1s peak, three peaks (CuO, Cu_2O and OH-) were used. The main peak analysis results are shown in Fig. 4. Based on the XPS peak area analysis, the atomic concentration of Cu surface was calculated using the equation below.

$$C_x = \frac{A_x / S_x}{\sum_k A_k / S_k}$$

C_x is an atomic concentration for an element X, A_x is a peak area, and S_x is a relative sensitivity factors (RSF). The relative sensitivity factors of 15.06, 1.8, and 2.93, were used for Cu, N, and O respectively. These factors were employed from CasaXPS database that normalized when C (carbon) = 1 [18]. The calculation results are shown in Table II, and the estimated stoichiometry of copper nitride in this study was close to Cu_4N. The reason for the Cu_4N formation than Cu_3N is possibly due to very slow chemical reaction at Cu surface with a long mean free path. Further investigation is necessary to understand a mechanism of Cu_4N formation. Cu_4N is known as a relatively metastable state in which copper atoms interstitially doped into the empty space of the cubic anti-ReO_3 crystal structure [19]. So, compared with Cu_3N, it has a better electrical conductivity [20-21] and a lower decomposition temperature that can provide pure Cu-Cu bonding at low temperature.

B. Optimization of two-step plasma treatment and evaluation of Cu bonding quality

In order to maximize the improvement of Cu bonding quality at low temperature, N_2 plasma treatment conditions were optimized using the RSM in DOE. Among the measured variables, Cu_4N and CuO peak area of $Cu2p_{3/2}$ profile and CuO peak area of O1s profile were selected as input variables for a response optimizer. Both the setup table and optimization plot are shown in Table III and Fig. 5. In the response simulator, the Cu_4N peak area was minimized and the CuO peak area was given a higher weight and importance. Because the antioxidant effect is the most important factor and the large amount of Cu_4N may not be necessarily for Cu bonding process. As a result, the optimized condition for N_2 plasma process to prevent copper oxidation was found to be 74W RF power, 3.7mTorr pressure, and 40seconds plasma treatment time.

The various Cu bonding interface images by SAT are shown in Fig. 6; (a) bonded at 400°C without any plasma treatment, (b) bonded at 300°C without any plasma treatment, (c) bonded at 300°C with two-step plasma treatment (the specimen from the center point condition in RSM), and (d) bonded at 300°C with the optimized plasma treatment condition. Even in the blanket Cu-Cu wafer bonding, it has been demonstrated that the wafer bonding with the optimized two-step plasma treatment showed a significant improvement in Cu bonded interface quality.

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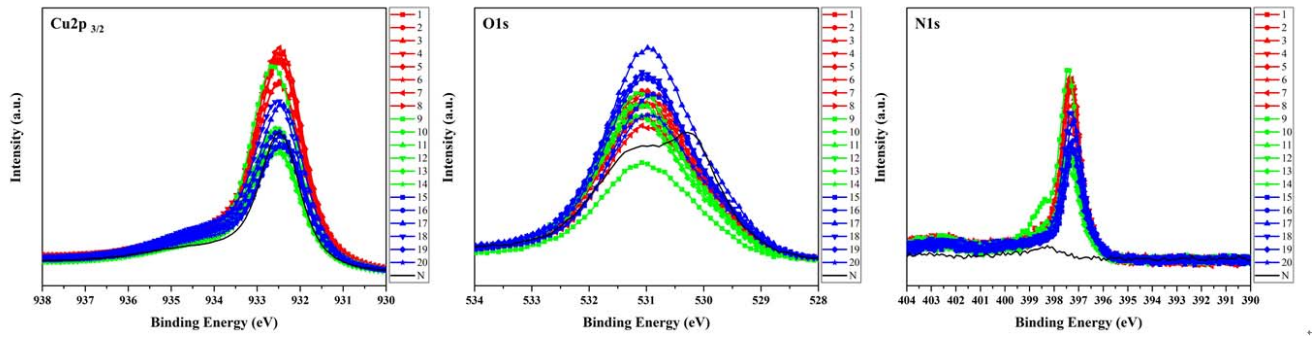

Figure 3. XPS profiles of each element (black solid line means non-plasma treated specimen)

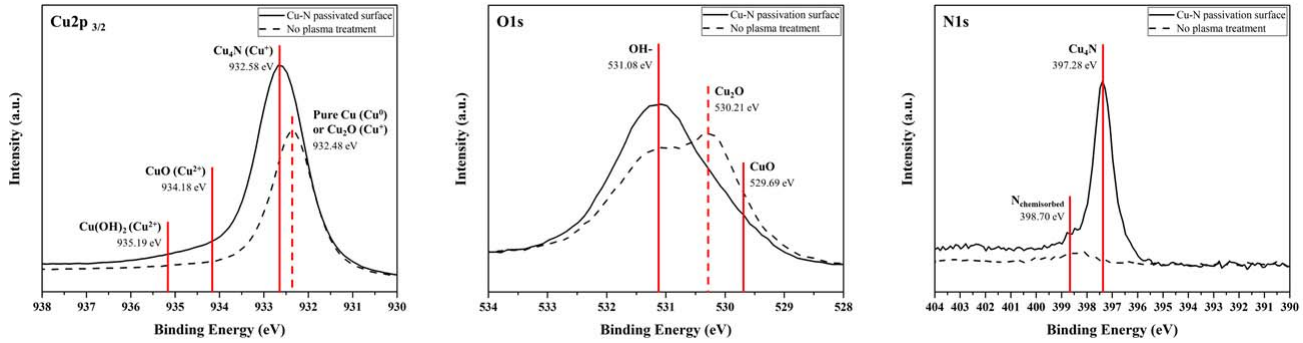

Figure 4. XPS peak analysis by deconvolution technique

TABLE II. STOICHIOMETRY CALCULATED BY DECONVOLUTION TECHNIQUE

Specimen No.	Cu (at.%)	N (at.%)	O (at.%)	Stoichiometry	Specimen No.	Cu (at.%)	N (at.%)	O (at.%)	Stoichiometry
1	78.4	13.4	8.2	$Cu_{4.71}N_{0.80}O_{0.49}$	11	76.6	12.8	10.6	$Cu_{4.60}N_{0.77}O_{0.63}$
2	77.3	11.0	11.7	$Cu_{4.64}N_{0.66}O_{0.70}$	12	75.8	12.4	11.8	$Cu_{4.55}N_{0.74}O_{0.71}$
3	78.3	13.2	8.5	$Cu_{4.70}N_{0.79}O_{0.51}$	13	76.0	13.0	11.0	$Cu_{4.56}N_{0.78}O_{0.66}$
4	77.1	12.7	10.2	$Cu_{4.62}N_{0.76}O_{0.61}$	14	76.2	11.8	12.0	$Cu_{4.57}N_{0.71}O_{0.72}$
5	76.3	13.0	10.7	$Cu_{4.58}N_{0.78}O_{0.64}$	15	73.4	12.5	14.1	$Cu_{4.40}N_{0.75}O_{0.85}$
6	77.8	11.6	10.6	$Cu_{4.67}N_{0.70}O_{0.64}$	16	73.9	11.4	14.7	$Cu_{4.43}N_{0.69}O_{0.88}$
7	77.7	12.7	9.6	$Cu_{4.66}N_{0.76}O_{0.57}$	17	75.5	11.4	13.1	$Cu_{4.53}N_{0.68}O_{0.79}$
8	77.8	11.2	11.1	$Cu_{4.67}N_{0.67}O_{0.66}$	18	75.9	11.8	12.2	$Cu_{4.55}N_{0.71}O_{0.73}$
9	78.7	15.9	5.4	$Cu_{4.72}N_{0.95}O_{0.32}$	19	74.1	11.0	14.9	$Cu_{4.45}N_{0.66}O_{0.89}$
10	77.1	11.9	11.0	$Cu_{4.63}N_{0.72}O_{0.66}$	20	74.2	12.2	13.6	$Cu_{4.45}N_{0.73}O_{0.82}$
Non	67.2	0.0	32.8	$Cu_{2.02}O_{0.98}$					

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TABLE III. RESPONSE OPTIMIZER SETUP TABLE

Response	Goal	Weight	Importance
[Cu2p$_{3/2}$] Cu_4N	Minimum	0.1	0.1
[Cu2p$_{3/2}$] CuO	Minimum	10	10
[O1s] CuO	Minimum	10	10

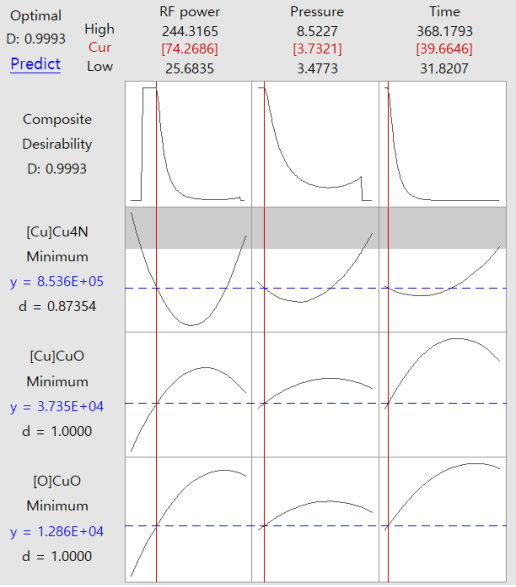

Figure 5. DOE optimization plot or copper nitride formation

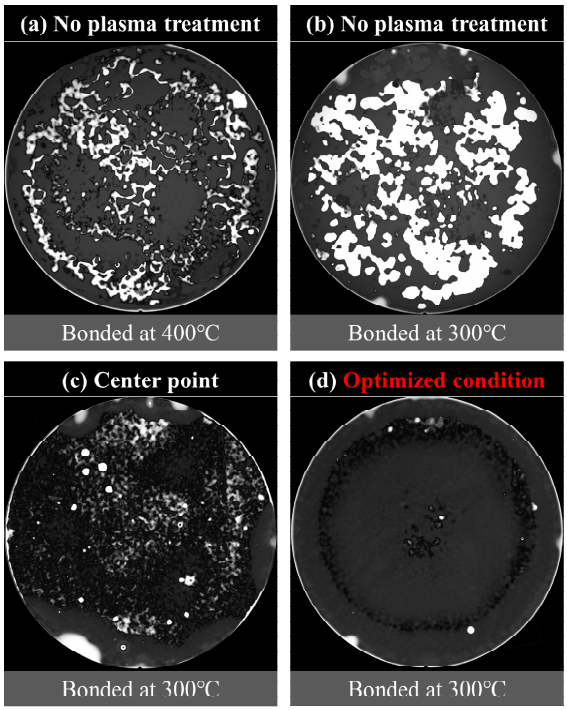

Figure 6. Cu-Cu bonded interface images by SAT: (a) bonded at 400ºC without any plasma treatment, (b) bonded at 300ºC without any plasma treatment, (c) bonded at 300ºC with two-step plasma treatment (the center point condition in RSM), and (d) bonded at 300ºC with the optimized plasma treatment condition

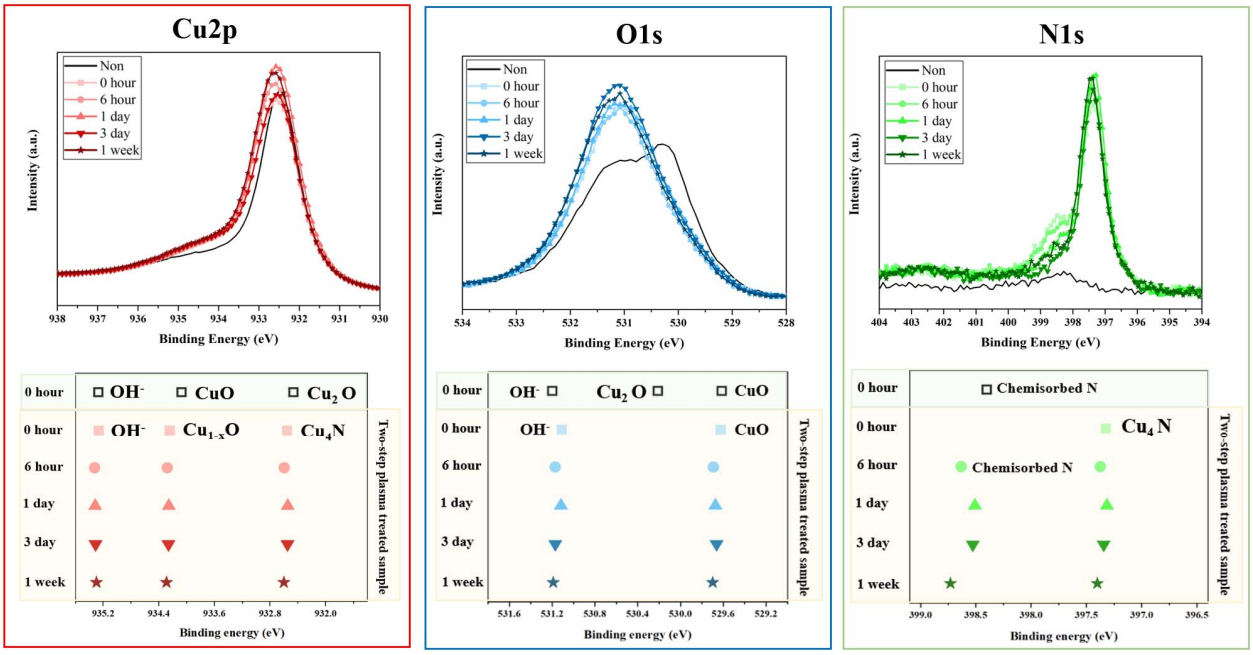

Figure 7. XPS analysis of copper nitride specimens aftter exposed to air from 0 hour to 1 week

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C. *Sustained effect of copper nitride passivation over time*

The sustained effect of copper nitride passivation layer was investigated over time for 0-hour, 6-hour, 1-day, 3-day, and 1-week in air. The specimens were prepared with the optimized plasma condition obtained by the RSM analysis. Each specimen was evaluated by XPS analysis and the results are shown in Fig. 7. No further oxidation (Cu_2O) was observed in all specimens, and the very small peak of CuO estimated by the O1s peak deconvolution was kept throughout. As seen in the N1s profiles, Cu_4N passivation layer was well maintained up to 1 week. It clearly showed that the copper nitride passivation prevented further oxidation and showed an excellent lifetime reliability up to 1 week in air.

IV. Conclusion

The optimization of N_2 plasma process in the two-step plasma treatment on Cu surface was studied for a low temperature Cu-Cu bonding. The N_2 plasma process condition was designed by the RSM based on a CCD in DOE methods. It has been demonstrated that the optimized N_2 plasma process in the two-step plasma treatment was significantly improved the Cu-Cu bonding quality bonded at 300°C. The copper nitride formed in this study was found to be Cu_4N, and this copper nitride passivation layer effectively prevents further oxidation up to 1 week in air.

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