OXYGEN-FREE PLASMA DESCUM PROCESS FOR PHOTOSENSITIVE CYCLOTENE™ POLYMER FOR WAFER-LEVEL CHIP SCALE PACKAGING

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BIOGRAPHY

Jeff (Jingjun) Yang, Ph.D., is a senior specialist of Advanced Electronic Materials at The Dow Chemical Company, and is responsible for developing applications of Cyclotene™ polymers in wafer-level packaging, integrated optoelectronics, and flat panel display areas. Yang earned a Ph.D. from Florida Atlantic University and a MS Technology in materials science and engineering from the Chinese Academy of Science &. Dr. Yang holds several patents, and has authored or co-authored over 30 papers in semiconductor processing, materials development and fracture mechanics.

Qingyuan Han, **Ph.D.**, is a senior scientist with Axcelis Technologies' Curing and Cleaning Systems, and a program leader responsible for low-k film process development. He has developed photoresist strip and residue removal processes for several low-k materials, and plasma curing technology for porous low-k materials. Dr. Han holds multiple patents related to semiconductor processing. He has an MS and a Ph.D. from the University of Minnesota (Twin Cities) in mechanical engineering.

ABSTRACT

A new plasma descum process, which uses no oxygen and a very small amount of fluorine, has been developed for BCB descum in a wafer level chip scale packaging application. This oxygen-free descum process employs forming gas (H_2/N_2) as its main etchant with a minimal amount of a fluorine containing gas (CF_4, < 0.5%). Addition of minimal amounts of CF_4 to the H_2/N_2 plasma increases BCB etch rate. The BCB etch rate increases linearly as temperature increases and can be finely tuned in the range of 150°C to 240°C. This oxygen-free plasma process has shown significant advantages over conventional oxygen-fluorine based plasma processes for descum of BCB polymers, including infinite etch selectivity of BCB over silicon oxide and silicon nitride, and no adverse impact to metals such as alumimum and copper alloys.

INTRODUCTION

Wafer level chip scale packaging (WL-CSP) has loomed as a new chip scale packaging (CSP) scheme that has not only created a true chip size package, but also extended the wafer fabrication process and test to the IC packaging level. This has rendered the IC packaging process being simplified, and the cost of IC packaging being reduced compared to current flip chip packaging. The photosensitive Cyclotene™ polymer, also known as benzocyclobutene (BCB), has been employed as both solder mask and redistribution dielectric materials for several commercial wafer level CSP platforms such as Ultra CSP™ [1], Xtreme™ CSP [2], Omega CSP™ [3], Shell BGA™ [4], chipCSP™, and the WL-CSP developed by IZM-TU Berlin [6]. A general review on wafer level CSP can be found in the reference [7].

Plasma descum is the final process step in integrating photosensitive BCB for wafer level CSP. Currently, this plasma descum process utilizes a gas mixture of oxygen and fluorine, more commonly either a mixture of 80% O_2 and 20% CF_4 or a mixture of 90% O_2 and 10% SF_6. Although no major issues have been reported on the oxygen-fluorine based plasma descum process for BCB polymer, there are some

limitations such as limited etch selectivity versus silicon oxide as well as against silicon nitride, and an additional cleaning process step (acetic acid cleaning) which is required for copper wafers after the oxygen-fluorine descum process. This study was aimed at finding an alternative plasma descum process which provides a more robust and cost-effective approach for the integration of photosensitive BCB.

Table 1: Properties of the Cyclotene™ Polymer

Property	Unit
Tensile strength	87 ± 9MPa
Tensile modulus	2.9 ± 0.2GPa
Elongation at break	8 ± 2.5
Poisson ratio	0.34
Residual stress on Si wafers	28 ± 2 MPa at 25°C
CTE	45 ppm/°C at 25°C
Glass transition temperature	> 350°C
Thermal conductivity	0.29 W/m°K at 25°C
Moisture absorption	< 0.2%
Dielectric constant	2.5 at 20 GHz
Dissipation factor	0.0008–0.002 at 1–20GHz
Breakdown voltage	3 x 10^6 V/cm
Volume resistivity	1 x 10^{19} Ω-cm
Optical loss	~0.2 dB/cm at 1320nm
Birefringence	< 0.001 at 850nm and 1320nm
Thermal-optical coefficient	~1.5 x 10^{-4}

EXPERIMENTAL

Benzocycobutene (BCB)-Cyclotene™ Polymer

The commercially available benzocyclobutene polymers [7] are partially polymerized (B-staged) benzocyclobutene monomers in the mesitylene solvent. The polymerization is a purely thermal process requiring no catalyst. When monomers or oligomeric benzocyclobutenes are heated to approximately 200°C, a highly reactive o-quinodimethane intermediate is formed which can polymerize rapidly by reaction with similar molecules, or by reaction with a variety of unsaturated functional groups. No volatile by-products are produced as a result of the polymerization, in contrast to polyimides which produce water as a by-product during the imidization. Table 1 summarizes various properties of the Cyclotene family of polymers. Special features that make BCB advantageous over other materials are: the low dielectric constant that is stable up to frequencies of 10 GHz (Fig.1), the low moisture absorption (0.2%) compared to polyimides (1% or higher) (Table 2), the high optical transmission over a wide range of wavelengths (Fig.2), and the high glass transition temperature (Fig.3).

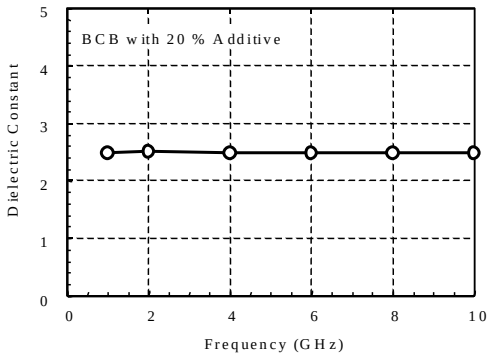

Fig. 1: Dielectric constant as a function of frequency.

Table 2: Moisture absorption of photosensitive BCB

Cyclotene™ Polymer	Thickness (μm)	Relative Humidity (%) 30	84
4024-40	5	0.061	0.14
4026-46	10	0.058	0.14
4026-46	20	0.050	0.14

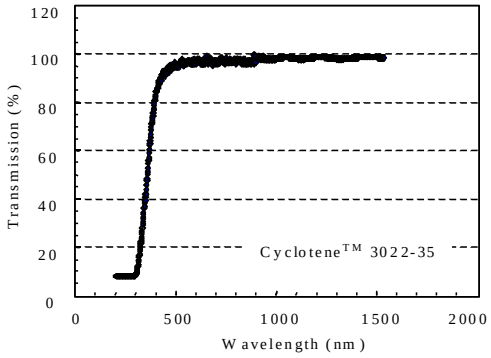

Fig. 2: Transmission spectra for Cyclotene™ polymer [8]

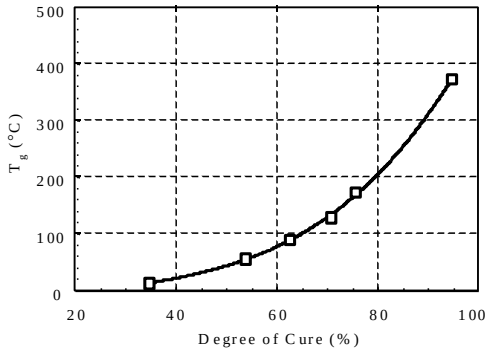

Fig. 3: Glass transition temperature as a function of the degree of cure for Cyclotene™ polymer

In addition, BCB provides significant advantages over other polymers for use as thin films in the electronic and optoelectronic industry. The BCB polymer can be fully cured at temperatures of 250°C or below, in contrast to polyimide which requires 350 - 400°C to achieve a complete cure. Figure 4 is a kinetics diagram or time temperature transformation diagram for BCB curing. The low temperature curing capability is of particular interest for GaAs or InP based integrated devices for wireless and fiber optic communications where thermal budgets of more than 300°C for 30 minutes may alter electrical or optoelectronic performance of the devices. As a result, BCB is dominantly employed in the GaAs and InP device fabrication as both interlayer and passivation dielectric material. The BCB polymer can also be snap-cured by means of a hot plate cure or rapid thermal process (RTP). Figure 5 shows the degree of cure as a function of hot-plate temperature for BCB polymers. In this experiment, the curing time (i.e. the time the BCB coated wafer is in contact with the hot plate) is only 20 seconds. For example, BCB polymer can be fully cured at 320°C in less than 1 minute. BCB also has excellent planarization capabilities. For example, Shimoto, et. al. [9] studied the degree of planarization (DOP) of BCB against polyimide and found that BCB provided much better planarization than polyimide for a given thickness ratio (defined as the thickness of the film divided by metal height), as shown in Figure 6.

Currently, several different grades of Cyclotene™ polymers are commercially available, which include the photosensitive 4000 series, the non-photosensitive 3000 series and a special non-photosensitive XU-71918.30 material, as summarized in Table 2.

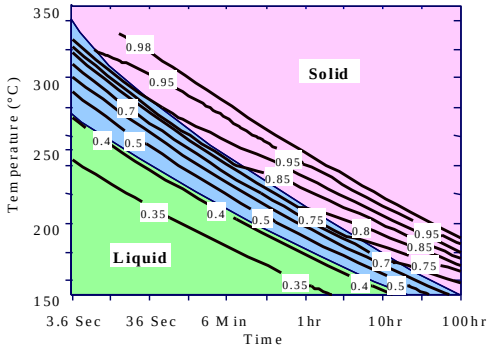

Fig. 4: TTT diagram for Cyclotene™ polymers.

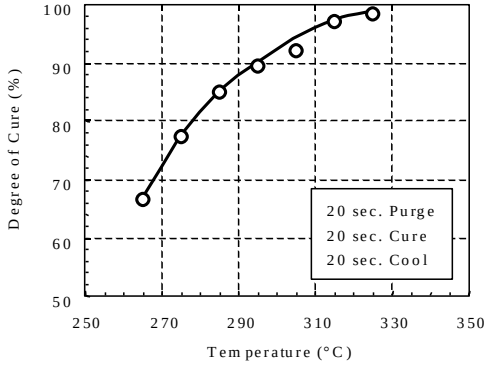

Fig. 5: The degree of cure versus hot-plate temperature for snap curing process for Cyclotene™ polymer.

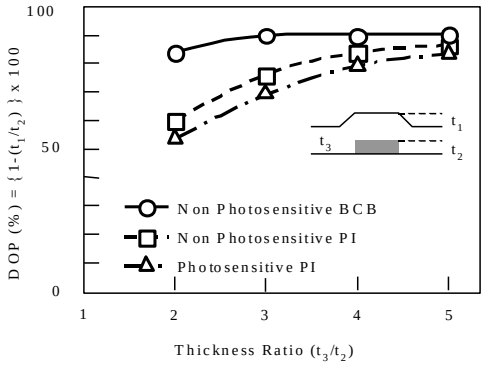

Fig. 6: Degree of planarization for BCB and PI [9].

Table 3: Commercially available Cyclotene™ Products

Cyclotene™ Product	Viscosity (cSt)	Thickness Range (µm)
XU-17918.30		
3022-35	14	1.0 – 2.4
3022-46	52	2.4 – 5.8
3022-57	259	5.7 – 15.6
3022-63	870	9.5 – 26.0
4022-35	195	2.5 – 5.0
4024-40	350	3.5 – 7.5
4026-46	1100	7.0 - 14

Photosensitive BCB Process

Figure 7 shows the process flow for photosensitive BCB polymers commonly used in applications such as wafer-level CSP. In this study the 4024-40™ resin was used. The detail for each of the processes is described below. An adhesion promoter – AP3000 was first spin-coated on wafers at 3000 rpm for 30 seconds, then the 4024-40 resin was coated at 2500 rpm for 20 seconds, followed by a soft bake at 80°C for 90 seconds. The film thickness after soft bake is about 7.1µm. After spin coat and soft bake, the film was exposed on a Karl Suss MA150 mask aligner through a via test mask at an exposure gap of 50µm, and an exposure dose of 200mJ/cm^2. Then, the exposed film was developed in a puddle develop procedure using a DS2100 developer. Prior to conducting the puddle develop process, the end-point of the developing time was determined on an unexposed wafer which had been subjected to the same processes as the test wafers except for the exposure. The total develop time for exposed wafers is 50% beyond the end-point. Following the develop process, the wafers were immediately baked on a hot plate at 70°C for 60 seconds. Then, the wafer was cured at 210°C for 40 minutes using a Blue-M. The oxygen level in the oven was maintained below 100ppm to avoid BCB oxidation.

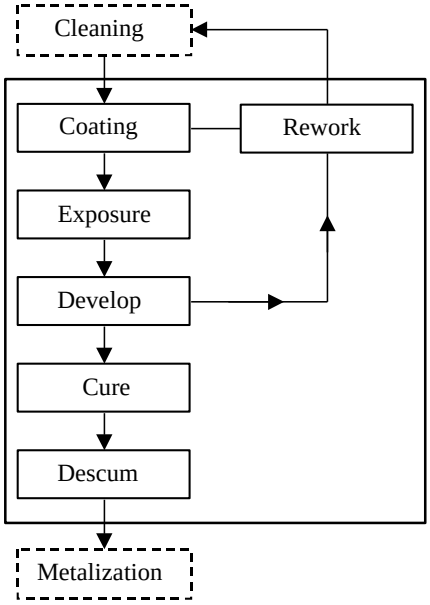

Fig. 7: The process flow diagram which is commonly employed for photosensitive BCB

Oxygen-Free Plasma Descum Process

The BCB descum experiments were conducted using an Axcelis 200mm plasma asher. This tool employs a downstream microwave plasma generator with a low volume reaction chamber, commonly used to remove photoresist and residues for both FEOL and BEOL chip manufacturing applications. The downstream microwave plasma provides the flexibility to

select different plasma chemistries during different process steps.

For the BCB descum application an oxygen-free plasma chemistry (N_2-H_2 forming gas with a small amount of CF_4) was used to avoid metal corrosion and BCB polymer degradation. Blanket coated and patterned BCB wafers were exposed to different plasma conditions. Film thickness of the BCB films before and after plasma exposures were measured using NanoSpec2100 and/or Prometrix SM200 film thickness metrology. The rate of BCB removal was calculated based on the time exposed to the plasma (which was 60 seconds in most cases) and the BCB film thickness removed. The targeted descum rate was 2000 – 5000 Å of the BCB film per minute.

RESULTS AND DISCUSSION

The Effect of Temperature

Earlier studies have shown that the etch rate of organic polymers under forming gas plasma is strongly dependent on wafer temperature. Therefore, in this study the wafer temperature was considered as one of the factors to control the BCB etch rate. Figures 8 and 9 present the current experimental results of etch rate as a function of temperature obtained with 100mm and 150mm patterned wafers, respectively. In both sets of experiments, the forming gas plasma process was conducted with and without CF_4 while the highest temperature was limited to 250°C considering the fact that BCB is usually cured at a temperature of 250°C or below. The other process conditions were: plasma power = 2000W; forming gas (H_2/N_2) flow = 3000sccm; chamber pressure = 1 torr; and plasma exposure time = 60 seconds. As expected, the BCB etch rate increases almost linearly with temperature, thus providing a large process window and flexibility in controlling the etch rate. It should be mentioned that the 100mm BCB wafer was placed on a 200mm bare silicon wafer during plasma exposure. This results in an actual temperature of the 100mm BCB wafer that is lower than the control temperature by approximately 30°C, and accounts for the difference in etch rate between the 100mm wafers (Fig. 8) and the 150mm wafers (Fig. 9) for a given temperature.

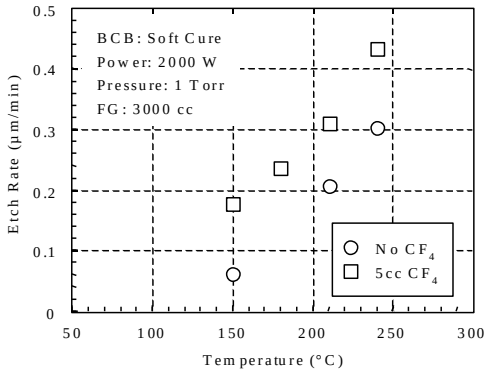

Fig. 8: BCB etch rate as a function of temperature with or without CF_4 obtained on 100 mm patterned wafers.

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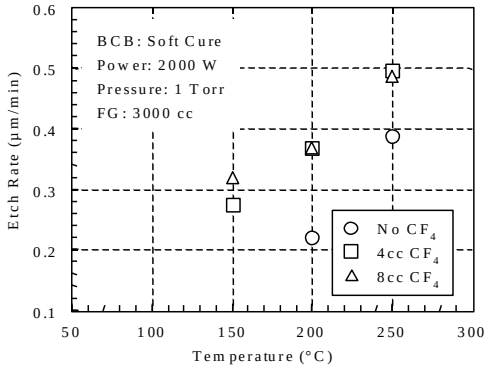

Fig. 9: BCB etch rate as a function of temperature with or without CF_4 obtained on 150 mm wafers.

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FTIR analyses conducted on the BCB surface after the forming gas plasma process showed no indication of BCB oxidation irrespective of the higher wafer temperature during the forming gas plasma process. However, a slight increase in the degree of BCB cure was observed if the wafer temperature was higher than the BCB cure temperature. Thus, it is recommended that for

the forming gas plasma process the wafer temperature should remain below the BCB curing temperature for applications where a controlled cure degree for BCB is desired.

The Effect of Fluorine (CF_4)

It is apparent from the results shown in Figures 8 and 9 that the addition of small amounts of CF_4 (less than 0.5 %) to the forming gas plasma will enhance the BCB etch rate for all process temperatures. The etch rate of BCB remains unchanged when the CF_4 concentration is increased from 4sccm to 8sccm, as shown in Figure 9. It was found that further increases in the CF_4 concentration in the H_2/N_2 plasma actually reduce the BCB etch rate. For example, when the CF_4 concentration was varied from 8sccm to 20sccm the BCB etch rate decreases by 25% (unpublished results).

Etch Selectivity of BCB versus Si_3N_4 and SiO_2

To further evaluate the oxygen-free plasma descum process, the etch selectivity of BCB versus silicon oxide and versus silicon nitride were tested. The oxide and nitride wafers were exposed to the same BCB descum process conditions, but for substantially longer time (10 minutes instead of 1 minute) in order to obtain a more accurate measurement. As shown in Table 4, the film loss of both oxide and nitride were negligibly small compared to the BCB removal rate. The etch selectivity of BCB over oxide and nitride, therefore, was virtually infinite.

Table 4: Oxide and Nitride Film loss Data

Etch Condition			Film Loss (Å)	
Temp (°C)	CF_4 (cc)	Etch Time (min)	Si_3N_4	SiO_2
180	5	10	-12.3	-1.5
210	5	10	-0.6	-0.1
240	5	10	5.8	0.6

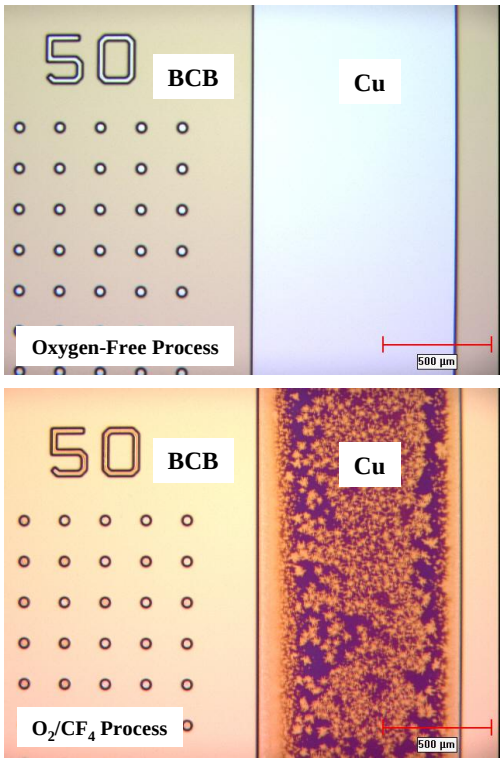

Fig. 10: Optical microscopy of Cu surface after descum showing severe corrosion of Cu after O_2/CF_4 plasma descum in contrast to a corrosion-free surface after O_2-free plasma descum.

The Effect of Oxygen-Free Plasmas on Metals

Both aluminmum and copper wafers were prepared with Cyclotene™ 4024 using the same processes as described previously. Then, one set of wafers was treated with the conventional O_2/CF_4 (80:20) plasma descum process, while the other set of wafers was processed with the oxygen-free plasma descum process (forming gas: 3000sccm; CF_4: 5 ccm; power: 2000W; pressure: 1 torr; and temperature: 180°C). The process time was 60 seconds for both. The wafers that have been processed with the oxygen-free plasma showed no visiual change (e.g., discoloring or change in reflectivity of the metal surface) on either metal surface (Cu or Al).

Comment [ILB3]: You should explain why the nitride results in film growth. Is this real (polymer deposition probably)? Also

However, the O_2/CF_4 plasma process resulted in a clearly visible oxidation of the copper surface and noticable loss of shininess on the aluminum surface. Figure 10 shows optical microscope pictures which were taken on the surface of the patterned wafers after the descum process, showing severe copper corrosion for the wafer processed with O_2/CF_4 plasma in contrast to the wafer processed with the oxygen-free plasma which demonstrated no difference before and after the descum process. It is because of this oxidation of the copper surface during the O_2/CF_4 plasma descum process that the wafers need to be cleaned with acetic acid immediately thereafter to remove the corroded copper surface and to avoid further growth corrosion. Since the oxygen-free plasma descum does not cause copper corrosion, the additional acetic acid cleaning process can be elminated.

The Effect of Oxygen-Free Plasma to the BCB

Surface analyses such as AFM and XPS were conducted to characterize the BCB surface after the descum process. Figure 11 presents AFM images of the BCB surface after various descum processes. No unusual surface features such as pitting were observed for both forming gas and O_2/CF_4 plasma processes. The BCB surface subjected to forming gas only (6.2nm) is rougher than the surface subjected to forming gas with CF_4 (4.6nm) which in turn, is slightly rougher than the surface subjected to O2/CF4 plasma (2.1nm).

CONCLUSION:

An oxygen-free (forming gas) plasma descum process was developed for photosensitive benzocyclobutene (BCB) polymer. The following conclusions are drawn based upon the current experimental results:

1. The etch rate of BCB tends to linearly increase with increasing temperature under forming gas plasma with or without a trickle amount of CF_4.

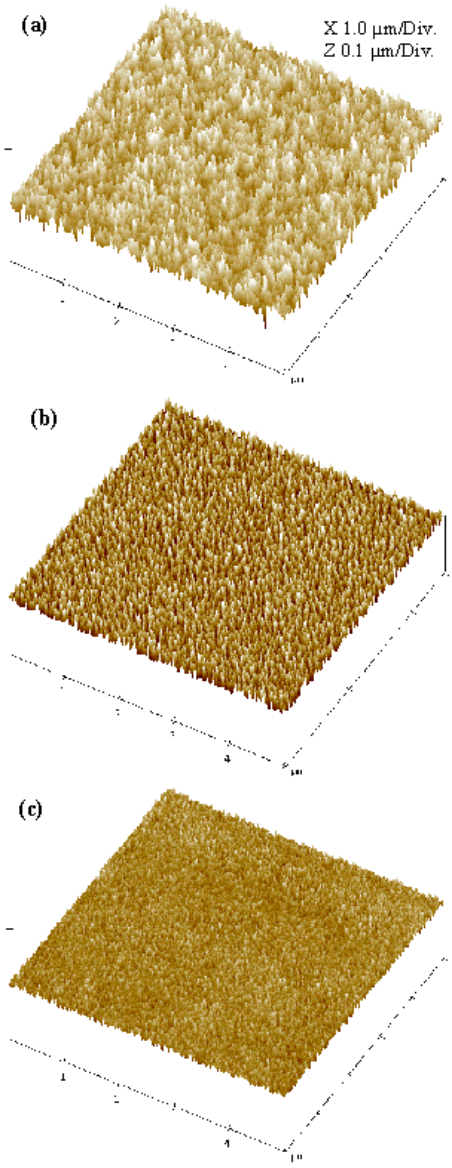

Fig. 11: AFM images of BCB surface after descum. (a): forming gas only; (b): forming gas with 4sccm CF_4; and (c) O_2/CF_4.

2. The addition of a trickle amount of CF_4 (less than 0.5%) into the forming gas significantly increases the etch rate of BCB.
3. Under the oxygen-free, low-fluorine plasma condition both nitride and oxide film loss are negligiable, therefore the etch selectivity of BCB against silicon nitride and silicon oxide is virtualy infinite.
4. This oxygen-free plasma process does not have any impact to copper, while O_2/CF_4 plasma interacts with copper to result in corrosion. A severe Cu corrosion often takes place during and after the O_2/CF_4 plasma process and hence an immediate acetic acid cleaning is necessary for O_2/CF_4 plasma. The oxygen-free plasma descum process does not require such an additional step.
5. Because of these advantages shown in this paper, the oxygen-free plasma process can be extended to BCB rework, particularly for fully cured BCB. We have not seen any wet chemicals which can effectively remove the BCB without inducing damage to metals and other dielectric materials.

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