Hydrophobic Self Assembly Molecular Layer for Reliable Cu-epoxy Interface

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Abstract

This paper discusses the use of a hydrophobic thiol based compound as adhesion promoter for copper (Cu)-epoxy interface. The motivation of this study is the long term reliability of the interface. In order to solve the moisture related reliability problem at the interface, thiol based molecules having hydrophobic characteristic (SAM N) is introduced at the interface. The rationale is to reduce the moisture uptake and hinder the diffusion into the interface. The thiol compound adsorbs onto a Cu substrate to form a self assembly molecular layer (SAM) through solution deposition. The SAM structure was designed to form covalent bonds with epoxy system while hydrophobicity was realized with long alkyl chains. The hydrophobicity of the surface treatment and wettability to epoxy adhesive was characterized using contact angle measurements with DI water and liquid epoxy. The wetting properties were shown independent of the treatment time. The results demonstrate selective wetting properties of the treatment. Water does not wet the treated surfaces (>110°) but the surfaces achieve good wetting with epoxy (<10°). Interfacial adhesion of the specimens prepared from modified substrates was bonded to epoxy and evaluated through a TDCB fracture test. In the reliability test, the Gic of the interface drops slightly from 45.7±5.5 Jm⁻² with freshly prepared specimens to 40.0±11.1 Jm⁻² with the moisture pre-conditioned ones. This indicates that with the SAM N treatment, the interfacial integrity is retained in long term service. The paper also discusses the hydrophobic behavior of the SAM N surface which enables long time storage of the pre-treated substrate under ambient environment. The paper introduces a new thiol based coupling agent which provides reliable Cu-epoxy interfaces.

Introduction

A general trend in electronic industry requires small package size, higher integration and increased system speeds. To align with this trend, the heat dissipation requirement for high density integrated circuit (IC) packages becomes increasingly important [1]. Copper (Cu)-based leadframes is a popular choice for leadframe material for its excellent thermal conductivity. However, it is known to have poor package reliability [2, 3]. The Cu leadframe generally exhibits poor adhesion with polymer encapsulant as compare to Alloy 42 leadframe [4]. In a plastic packages, epoxy compound are usually employed as encapsulating materials for their excellent insulating and mechanical properties. Nevertheless, the poor bondability to epoxy makes the copper leadframe package fails during its service life or even in its manufacturing process.

Several approaches [5-7] have been taken to obtain higher adhesion strength between Cu and EMC. The most common approach was copper oxidation. Chemical oxidation through acidic or alkaline solution is preferred over thermal method because the morphological modification obtained from chemical method gives better adhesion [8]. The chemical modification enhances surface roughness of the substrate. It provides more attachment sites which interlock mechanically with the polymer. With the optimized condition, the interfacial adhesion has been enhanced from almost zero to 100 Jm⁻² in Lee’s study [9].

Kim et al. [10] reported the reliability issue for the black oxide treatment. The button shear strength of oxide treated samples dropped from 7.5 MPa to 6.5 MPa under thermal cycle at -50°C to 150°C for 1000 cycles while it was reduced to 1.27 MPa at a pressure cooker test (121°C/100% RH for 120 hours). The finding implies that the moisture rather than extreme temperature has a more significant effect on the package reliability. The study suggests the need for tackle the moisture induced problem at Cu-epoxy interface.

Several groups attribute the cause of interfacial delamination in a Cu-epoxy joint to moisture uptake of the epoxy polymer and relate the interfacial adhesion to the diffusion of moisture along the interface. Yee et al. [11] have recommended the hydrophobic component in an epoxy system can hinder moisture uptake of the bulk epoxy. It implies that a hydrophobic interface may reduce the moisture content at an interface. Kinloch [12] suggested that the long alkyl chain of an vinyl silane with 20 carbons might impede water and improve bond durability. The argument is that the middle alkyl chains which are highly hydrophobic can obstruct water penetration and can thus improve the interface. These studies suggest a hydrophobic Cu-epoxy interface may improve the long term reliability of an interfacial joint.

One of the possible solutions is to introduce non-polar interfacial molecules to the system. The hydrophobic characteristic of the non-polar group can hinder interfacial moisture diffusion and water residence at the interface. To create hydrophobic interface in Cu-epoxy system, hydrophobic coupling agent originated from thiol based molecules is proposed. The thiol molecules react readily with Cu atoms, can build a strong (chemically bonded) self assembly molecular layer on the Cu surface. These direct Cu-S linkages can prevent premature failure happen at the interface.

This paper aims at developing a hydrophobic thiol based self assembly molecular layer (SAM N) on a substrate so as to
improve the adhesion of the Cu-epoxy interface under long term reliability test. The study starts with discussing the parametric influence of treatment time in formation of an adhesion promoting layer on a Cu substrate. Copper substrates were modified by a 0.1mM thiol solution in different treatment times. To understand the hydrophobicity of the SAM N treatment, water contact angle was evaluated. The substrate was then bonded with an epoxy encapsulate. Interfacial adhesion of the SAM N modified specimens was evaluated by measuring fracture toughness (GIC) of the interfaces using tapered double cantilever beam (TDCB) test. The fresh GIC data was used to choose the most suitable treatment time in preparing substrates for the reliability test.

A hydrophobic surface benefits adhesion by protecting the surface from contaminants. Due to the low surface energy, hydrophobic surfaces are less prone to water, inorganic gaseous and volatile hydrocarbons. The surfaces are more stable and inert in attracting adhesion inhibitors. The hydrophobic surfaces are thus capable for long time storage before adhesive application. In studying the long time storage behavior of the treatment, both water and epoxy contact angle for substrates under different storage conditions was inspected. Epoxy wetting test can give a preliminary indication for good adhesion of an interface [13]. A small contact angle ensures intimate contact of the adhesive to the metal surface. Chemical reaction can be realized readily when adhesive and substrate comes into intimate contact. Strong interfacial adhesion is expected when bonding has been achieved at the interface. The influence of storage conditions on the hydrophobicity and wettability to epoxy was investigated. To study the impact on interfacial adhesion, SAM N treated substrates stored in humid environment was bonded to epoxy and evaluated in TDCB test.

In the reliability test, 85°C/85% RH pre-conditioning was adopted. GIC measurement was conducted. The impact of hydrophobic interface to the interfacial integrity under reliability test is discussed in this study.

**Experimental**

A. Materials

To investigate the hydrophobic behavior and the adhesion of the modified substrate, three types of substrate were used in this study. C194 Cu based leadframe was employed as substrate for surface compositions analysis and the morphological study. Sputtered Cu substrates having 50ÅTiW+5000ÅCu on (100) wafer was used in the contact angle investigation. In the interfacial adhesion study, fracture test was conducted using tapered double cantilever jig machined form red brass. The nominal composition of the Cu leadframe and red brass substrates was evaluated by X-ray fluorescence spectrometer (XRF) model JSX-3201Z from JOEL. The composition of C194 leadframe and the red brass jig was Cu-2.2Fe-0.08Si-0.48Zn-0.06Sn (wt%) and Cu-0.05Si-0.38Zn-0.02Sn (wt%), respectively, which were chemically similar.

In order to produce hydrophobic surface on Cu substrate, a long alkyl-chain thiol, 11-aminoundecanethiol, hydrochloride (SAM N) purchased from Dojindo Laboratories, was used. Fig. 1 illustrates the chemical structure of this thiol. The long alkyl chain provides hydrophobic properties of the SAM structure while the amine end group aims at reacting with epoxy to ensure a strong joint. The SAM structure was built onto the Cu substrate through solution deposition.

\[ \text{HS}-(\text{CH}_2)_n-\text{NH}_2 \text{ HCl} \]

**Fig. 1 Chemical structure of the thiol molecules used in this study**

The adhesive adopted in the test is Hysol® FP4526, a commercially available underfill obtained from Henkel Loctite. It is a low viscosity, fast flow epoxy based material designed for capillary underfill on flip chip application.

B. Surface preparation

The thiol was used as received. It was dissolved into absolute ethanol (~96% purity, Aldrich) and diluted to 0.1mM solution. All types of the substrate were cleaned with anti-grease solvent followed by Fry 90 flux (Fry Technology) to reduce surface oxide. To further eliminate carbonate and hydroxide on the Cu surface, the samples were immersed into acetic acid for 10min before solution deposition. In studying the process window of SAM N treatment, the thiol was adsorbed onto the pre-cleaned Cu surface from a pre-mixed solution for 1 to 48 hours. The treated substrate was then removed from the solution and rinsed thoroughly with ethanol before blow drying with nitrogen.

C. Surface characterization

Upon deposition, the existence and quality of the SAM modified surface has been characterized by surface analysis techniques. Detailed descriptions are written below.

**Scanning Electron Microscope (SEM)**

The surface topography of the SAM treated sample was evaluated by a SEM 6700F from JEOL Ltd. The electron microscope was operated under 5-15kV in secondary electron (SE) mode. Images under high magnifications were taken to reveal the morphology, feather size and coverage of the modified layer.

**X-ray Photoelectron Spectroscopy (XPS)**

To investigate the surface composition and the bonding of the treated substrate, XPS, model 5600 multi-technique system bought from Physical Electronics, was utilized. A monochromatic AlKα X-ray source was run at 1486.6eV. The spot size was kept at 600μm for all sample studied in this paper.

D. Hydrophobicity of the SAM N treated substrate

In the hydrophobicity test, DI water contact angle on the SAM treated samples was measured using the sessile drop method with a goniometer (DIGIDROP, GBX). A sessile droplet of about 20μl DI water was dispensed onto the sample Cu substrates. The measurement was carried out at different period of time after SAM treatment. In the long time storage test, the as-deposited contact angle was compared with that stored at lab environment after 2 days, 1 week and 4 months. Hydrophobic samples stored in extreme humid condition of 30°C/85%RH for 1 week was investigated.
E. Wetting to epoxy

Contact angle measurement was conducted using goniometer (DIGIDROP, GBX). About 10µl epoxy underfill (Henkel Loctite Hysol FP4526, the same underfill applied in the TDCB test) was dispensed onto on the sample Cu substrates. Due to the viscoelastic behaviour of the underfill, the contact angle reduced with time. The contact angle measurement was therefore taken after 30min waiting time. The epoxy contact angle on treated samples after different storage time was reported.

F. Interfacial adhesion evaluation

To determine the interfacial adhesion of the Cu-epoxy joint, fracture toughness (GIC) of the modified joint with Tapered Double Cantilever Beam (TDCB) testing specimens was measured according to ASTM D3433. The specimen was prepared from epoxy underfill sandwiched between a pair of tapered Cu jig. The tapered geometry guarantees a constant moment during the crack growth. To ensure that crack opened at the right interface, a 60mm precrack was introduced in the front end of the testing jig. 0.5mm thick epoxy underfill was cured between the two jigs at 80°C for 6 hours. The width and total length of the jig was 7mm and 102mm respectively. Fig. 2 shows a schematic diagram for the TDCB configuration.

\[
G_{IC} = \frac{4P^2(3a^2 + h(a)^2)}{EB^2h(a)} \quad \text{Eq. 1}
\]

where 
- \(P\) is the critical load for stable crack opening,
- \(B\) is the width of the specimen,
- \(a\) is the crack length
- \(h\) is the corresponding thickness of the jig at the point of crack front

\[
m = \frac{3a^2 + h(a)^2}{h(a)^3} \quad \text{Eq. 2}
\]

where 
- \(m\) is a constant for the tapered jig which is determined by the jig geometry.

G. Reliability test

Interfacial integrity of the Cu-epoxy joint was measured with pre-conditioned bonded TDCB specimens. In order to review the impact of the hydrophobic treatment to reliability, two types of SAM treatment was adopted: SAM Y (hydrophilic) and SAM N (hydrophobic). The SAM Y substrates was prepared from 5mM SAM Y solution treated for 48 hours while the SAM N was prepared from 0.1mM SAM N solution for 48 hours. After bonded with the epoxy underfill, the TDCB specimens was pre-conditioned inside a humidity chamber set at 85°C with 85% RH for 168 hours. The specimens were then taken out for the interfacial adhesion test. The interfacial integrity was evaluated as percentage decrease in adhesion upon aging.

Result

A. Surface analysis of SAM N treated substrate

Surface morphology

Fig. 3 shows the surface morphology of the thiol treated Cu surface under SEM. The thiol modified the Cu with needle-like features. The irregular needles bundle together covering the whole substrate surface.

Surface adsorption of the thiol molecules

Fig. 4 illustrates the XPS spectra for a control substrate and a substrate treated with SAM N solution. Table 1 reports the atomic composition of the two samples. In comparing with the control spectrum, significantly higher C, N, S content has been measured from the treated sample. The detection of these elements indicates thiol molecules are presence on the Cu surface.

Fig. 3 SEM microscopy of Cu substrates: control without treated (left); SAM N treated (right)

Fig. 4 XPS spectra for a control (top) and a SAM N treated sample (bottom)
Table 1 Atomic percentage of elements on sample surface

<table>
<thead>
<tr>
<th>Element</th>
<th>control</th>
<th>0.1mM SAM N</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>40.12</td>
<td>60.21</td>
</tr>
<tr>
<td>N1s</td>
<td>0.16</td>
<td>2.79</td>
</tr>
<tr>
<td>O1s</td>
<td>27.41</td>
<td>16.90</td>
</tr>
<tr>
<td>S2p</td>
<td>0.24</td>
<td>2.85</td>
</tr>
<tr>
<td>Cl2p</td>
<td>1.16</td>
<td>2.45</td>
</tr>
<tr>
<td>Cu2p3</td>
<td>30.91</td>
<td>14.80</td>
</tr>
</tbody>
</table>

High resolution XPS spectrum for S2p peak is shown in Fig. 5. From the S2p spectrum, a broad peak was observed at ~163.8eV. As reviewed in literature [14, 15], chemisorbed S should give S2p peak at ~162eV. The spectrum suggests that chemically bonded thiols are present on the substrate.

B. Hydrophobicity of the prepared substrate

Water contact angle of the SAM N treated substrate in different treatment times is given in Fig. 6. Without SAM N treatment, the substrates are hydrophilic with a small contact angle at 67.5±3.9°. The contact angle increases tremendously to larger than 110° upon SAM N treatment regardless of the treatment times. The measurement suggests hydrophobic surface is obtained after the SAM N treatment.

C. Processing window for the SAM N treatment

In order to study the appropriate treatment procedure for formation of SAM N on Cu substrate, process parameter in terms of treatment time from 0.1mM SAM N solution was conducted. Fracture toughness (GIC) of the surface modified Cu jig was examined. A control Cu specimen without any treatment was used as a benchmark. Typical force curves for the control and treated sample were given in Fig. 7. The average critical load for stable crack propagation for control and 0.1mM_48hr specimen was 39±3N and 128±2N respectively.

GIC was calculated from the critical load needed for propagating a stable crack according to Eq. 1. Fig. 8 summarizes the GIC results of the control and the SAM N treated Cu-epoxy interface in different treatment times. The results demonstrate that with the thiol treatment, the interfacial adhesion for Cu-epoxy improves significantly. Fracture toughness of Cu-epoxy is boosted from 4.8±0.8Jm⁻² to 65.4±13.3Jm⁻² after one hour treatment. The GIC reaches a maximum with 2 hours treatment to 95.2±20.2Jm⁻². The trend does not continue to climb, but drops to 70.5±12.2Jm⁻² to 54.0±11.2Jm⁻² with 4 hours and 18 hours treatment respectively. The lowest GIC is obtained from the 48hours specimen with 45.7±5.5Jm⁻². Although the GIC declines with this specimen (0.1mM_48hr), it achieves a nine fold improvement when compares with the control. With the weakest interface measured from this treatment time (48 hour), samples prepared from this treatment time were used for the long time storage and the reliability study described below.
D. Long time storage properties

Surface morphology

The morphology of the treated substrate after long time storage is shown in Fig. 9. Needle-like structure was formed on the substrates. No observable morphological change is found on the substrates stored either in lab or humid environment.

![Fig. 9 Morphological images of Cu surface treated with SAM N for as deposited (left), stored for 1 week (middle) and stored for at humid environment for 1 week (right)]

Hydrophobicity

Fig. 10 gives the hydrophobic properties of the treated substrates under different storage conditions. The corresponding contact angle images for the given substrates are given alongside. The water contact angle remains large with higher than 110° at the prolonged storage conditions. The substrates are hydrophobic. It implies that the substrate surfaces are less prone to contaminants.

![Fig. 10 Water contact angle of SAM N treated substrates in different substrates storage conditions (all substrates were prepared in 48 hours treatment time)]

Wetting to epoxy

The wetting properties of epoxy underfill on the prolonged stored SAM N treated substrates is illustrated in Fig. 11. Small contact angle with less than 10° was recorded from all substrates under long storage for up to 4 months in lab environment. About 8° was measured with substrates stored in a humid chamber at 30°C/85%RH for one week. Good wetting maintains after long time storage of the substrates. It indicates the substrates have not deteriorated and are ready for bonding after the storage.

![Fig. 11 Epoxy contact angle of SAM N treated substrates in different substrates storage conditions (all substrates were prepared from 48 hours treatment times)]

Interfacial adhesion

The influence of long time storage of the SAM N treated substrate on interfacial adhesion of the Cu-epoxy joint are described in Fig. 12. In exposing the 0.1mM_48hr substrates under 30°C/85% RH humid environment for one week, the GIC was measured as 50.4±0.7 Jm−2 which was comparable to the freshly bonded one. The test suggests that no adverse contaminate is adsorbed on the treated substrate. The interface is not weakened under long time storage in humidity.

![Fig. 12 Fracture toughness (GIC) of Cu-epoxy interface prepared from 0.1mM_48hr SAM N substrates that was bonded: 1) freshly after deposition (fresh) and 2) after stored in humid condition (30C/85%) for 1 week]

E. Reliability of the treated substrate

Fig. 13 illustrates the reliability impact on the interface integrity for the SAM N treated substrate. A slight drop on
GIC from 45.7±5.5Jm⁻² to 40.0±0.7Jm⁻² was recorded in the freshly prepared specimens and those aged in 85%/85%RH humidity chamber for 168 hours.

![Graph showing GIC (Jm⁻²) vs. Reliability test condition](image)

**Fig. 13** Impact of reliability test (85°C/85%RH for 168 hours) on GIC of the Cu-epoxy interface prepared from 0.1mM 48hr SAM N substrates. The GIC were compared with the freshly prepared SAM N specimens.

**Discussion**

Selective wetting behavior

Selective wetting properties of the treatment have been demonstrated by the contact angle measurement of the SAM N treated Cu substrates. The modified surfaces are non-wetting to water but they wet well with the epoxy underfill. The phenomenon may be explained by the molecular motion of the long chain thiol molecules when interacting with different liquids as described in Fig. 14. The SAM N molecules consists a thiol head group (bonded to Cu substrate) and an amine end group connected by alkyl chain of 11 carbons. Due to chemical nature, amine is hydrophilic while long alkyl chain is hydrophobic [16]. This gives distinct wetting behavior of the surfaces when interacting with the two liquids.

In contacting with water, the molecules minimize surface energy of the substrate by hiding the reactive amine group from water. This results in a large water contact angle at about 110°. While interacting with epoxy compound, the chains extend and expose the amine groups to the epoxy about 110°. While interacting with epoxy compound, the chains extend and expose the amine groups to the epoxy about 110°. This results in a large water contact angle at 40.0°. The phenomenon may be explained by the molecular motion of the long chain molecules when interacting with two liquids.

Table 2 lists the percentage decrease in adhesion for different systems. According to Ferguson’s study [18], a drastic deterioration in adhesion of 58.1% was recorded for interface without any treatment. The finding indicates that there is a need in improving the interfacial integrity of the Cu-epoxy interface under humid environment. Takano, et al. [19] and Kim, et al. [10] demonstrate the interfacial integrity of the black copper oxide treatments under aging test. A decrease of 83.1% was reported by Kim, et al. when the black oxide samples were aged in a 121°C/100%RH chamber for 120 hours. With the oxide samples pre-conditioned under 85°C/85%RH, 168hr, Takano, et al. demonstrated a decrease of 41.7% in a button shear test. The study indicates inefficient moisture resistance of the black oxide treatment to its insensitive handling procedure. Conventional surface treatment procedures require bonding of a treated substrate to an adhesive as fast as the treatment process. This is to prevent the organic or airborne contaminants from adsorbing onto the substrate that can deteriorate the interfacial adhesion. Due to their hydrophobicity, the SAM N substrates are less prone to attract contamination. It allows long time storage of the pre-treated substrates even under humid environment without worsen the adhesion.

Interfacial integrity under reliability test

The reliability results of the Cu-epoxy interfaces modified with SAM N treatment was compared with the untreated system and the black oxide treatment. The percentage decrease in adhesion after pre-conditioning represents the resistance of interfaces to the aging condition. The percentage of decrease in adhesion was calculated as Eq.3:

\[
\text{% decrease in adhesion} = \left(\frac{\text{adhesion before aging} - \text{adhesion after aging}}{\text{adhesion before aging}}\right) \times 100\%
\]

**Eq.3**

The hydrophobic behavior of the SAM N surface treatment is found advantageous to the surface treatment due to its insensitive handling procedure. Conventional surface treatment procedures require bonding of a treated substrate to an adhesive as fast as the treatment process. This is to prevent the organic or airborne contaminants from adsorbing onto the substrate that can deteriorate the interfacial adhesion. Due to their hydrophobicity, the SAM N substrates are less prone to attract contamination. It allows long time storage of the pre-treated substrates even under humid environment without worsen the adhesion.

Long time storage capability

The hydrophobic behavior of the SAM N surface treatment is found advantageous to the surface treatment due to its insensitive handling procedure. Conventional surface treatment procedures require bonding of a treated substrate to an adhesive as fast as the treatment process. This is to prevent the organic or airborne contaminants from adsorbing onto the substrate that can deteriorate the interfacial adhesion. Due to their hydrophobicity, the SAM N substrates are less prone to attract contamination. It allows long time storage of the pre-treated substrates even under humid environment without worsen the adhesion.

![Diagram explaining selective wetting capability of the SAM N treated substrates to water and epoxy](image)

**Fig. 14** Schematic diagram in explaining the selective wetting capability of the SAM N treated substrates to water and epoxy

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Upon aging of the SAM N treated specimens in 85°C/85%RH for 168hours, the GIC declines from 45.7±5.5Jm⁻² to 40.0±5.5Jm⁻² which results a 12.4% decrease
in adhesion. Significant interfacial integrity is retained in these specimens in comparison to the black oxide ones.

**Table 2** Percentage decrease in adhesion (calculated by eq. 3) for substrates in different treatments after preconditioning

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Sample</th>
<th>Test method/ unit</th>
<th>% decrease in adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treatment</td>
<td>Cu/UF</td>
<td>4-pt bending/ Jm²</td>
<td>58.1</td>
</tr>
<tr>
<td>Oxide#</td>
<td>Cu/EMC</td>
<td>BST/ MPa</td>
<td>83.1</td>
</tr>
<tr>
<td>Oxide</td>
<td>Cu/EMC</td>
<td>BST/ MPa</td>
<td>41.7</td>
</tr>
<tr>
<td>SAM N</td>
<td>Cu/UF</td>
<td>TDCB/ Jm²</td>
<td>12.4</td>
</tr>
<tr>
<td>SAM Y</td>
<td>Cu/UF</td>
<td>TDCB/ Jm²</td>
<td>28.4</td>
</tr>
</tbody>
</table>

* All the tests except “Oxide #” were pre-conditioned for 85°C/85%RH, 168hr
* Oxide # was pre-conditioned for 121°C/100%RH, 168hr

**Hydrophobic contributions to the reliability**

To investigate the contribution of the hydrophobic character of the SAM N substrates to the reliability of the interface, another types of thiol (SAM Y) having hydrophilic characteristic was put under examination. The water contact angle of the SAM Y treated substrates was measured as 49.1±4.6°. The interface integrity of the hydrophilic specimens was tested after pre-conditioning under 85°C/85%RH for 168hours. Fig. 15 shows the GIC of the SAM Y specimens after pre-conditioning and compared with the freshly prepared one. Under the aging condition, the GIC decreases from 139.6±16.5Jm⁻² to 99.9±34.0Jm⁻².

**Conclusions**

A new thiol based coupling agent is introduced in this paper. The outstanding adhesion promoting characteristic of this coupling agent is summarized as follows:

1. The interfacial adhesion is enhanced from $4.8±0.8$ Jm⁻² to $95.2±20.2$ Jm⁻² after two hour SAM N treatment which is comparable to the value obtained from the black copper oxide treatment [9].

2. The hydrophobic behavior of the SAM N surface enables long time storage of the pre-treated substrate under ambient environment.

3. The interface integrity of Cu-epoxy under the SAM N treatment is resistance to moisture with only 12.4% decrease in GIC when compares to the freshly prepared specimens.

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**References**


