

High-Temperature Reliability of Copper Wire-Bonded Packages Encapsulated with Mold Compounds Containing Sulfur Compounds

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Abstract—Cu wire-bonded (CuWB) packaging is more susceptible to corrosion than traditional inert gold wires. CuWB reliability greatly depends on the compatibility of Cu wire with the surrounding encapsulating mold compound as this matrix can provide a corrosive environment leading to reliability issues. Many mold compounds contain specific components, which are sulfur-based compounds. Since the reliability testing of an encapsulated packaged device involves thermal treatments, such as the high-temperature storage life (HTSL) test, there is a concern that corrosive sulfur compounds can be produced at high temperatures (e.g., 150°C and 175°C), endangering CuWB reliability. This article describes detection methods of sulfur compounds produced from mold compounds, if any, at high temperatures such as 175°C and CuWB die package reliability with mold compounds containing sulfur compounds. The dynamic headspace concentration-gas chromatography-mass spectroscopy analysis technique was used to test liberation of gaseous and volatile sulfur compounds from mold compounds at temperatures 25°C, 150°C, 175°C, and 200°C. No gaseous sulfur compounds were detected by chromatographic methods within the time period of the experiments. To determine sulfur-containing anionic species present in the mold compound matrix, such as sulfide, sulfite, sulfate, and thiosulfate, ionic compounds were extracted to water and analyzed by ion chromatography. Upon analysis, the only sulfur-bearing anion found in the samples was sulfate. Thermally treated mold compounds for 2,000 h at 150°C and for 1,000 h at 175°C were also extracted and analyzed to determine possible decomposition of sulfur compounds due to the thermal aging process. Corrosion due to sulfur compounds and reliability of CuWB was evaluated by HTSL for 2,000 h at temperatures of 150°C and 175°C with devices packaged with mold compounds containing sulfur compounds. CuWB ball bond-Al interface and Cu stitch bond integrity were evaluated by focused ion beam-scanning electron microscopy with energy-dispersive x-ray spectroscopic analysis and wire pull and ball shear testing of CuWB ball bonds. No reliability issues due to sulfur compounds were found with mold compounds containing sulfates up to ~45 ppm.

Keywords—Copper wire bond, mold compounds, high temperature reliability, corrosion, electronic package

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INTRODUCTION

Replacement of gold wire by Cu for wire bond packaging of semiconductor devices generated several reliability concerns as Cu is more susceptible to corrosion [1-7]. Failures of copper wire-bonded (CuWB) structures caused by corrosive ions such as chloride were well described by several authors [8-11]. Encapsulation material such as mold compound was identified as a main source of corrosive ions. Corrosive failures associated with halide ions (Cl^- and Br^-) present in mold compounds were reported to be triggered by preferential attack of Cu-Al intermetallic compounds (IMCs). As in any corrosion process, several factors, such as presence of appropriate electrolytes, pH, and temperature, are important in deciding the extent of corrosion occurring at the Cu-Al interface. Generally, aggressive conditions such as highly accelerated temperature/humidity stress tests are required to cause corrosive opens at the Cu-Al interface. Typically, halide-based corrosion is not observed on copper wire itself.

Mold compounds are complex formulations containing several components capable of generating organic and inorganic species that can be potentially detrimental to the CuWB reliability. Many of them contain chemical components, generally sulfur-containing compounds, to improve adhesion to lead frames and resin to fillers. Stability of these sulfur compounds was suspected as a major concern because of the possibility of the compound's decomposition at higher temperatures to produce corrosive gases like SO_2 , SO_3 , H_2S , etc., or corresponding anions in presence of moisture. Many of these sulfur compounds are known to be corrosive to copper itself. If it happens, when package devices are subjected to various high-temperature reliability tests such as high-temperature storage life (HTSL) at $\geq 150^\circ\text{C}$, it can lead to corrosive failures. These failures can be due to corrosion of copper wire itself or at the Cu-Al IMC-Cu interface.

To understand potential risk due to sulfur compounds, it is important to determine whether sulfur-containing gaseous or ionic products are produced at high-temperature conditions between 150°C and 200°C. Secondly, extensive HTSL tests need to be conducted with encapsulated dies at high temperatures to assess possible corrosion of the CuWB devices, if any. Currently, studies to determine the level of sulfur compound formation and subsequent corrosion of packaged devices are very limited. This article describes chemical analysis methods to determine sulfur compounds produced, if any, at high

temperatures up to 200°C. Studies were conducted to understand high-temperature stability of adhesion promoter-containing mold compounds. In addition, packaged devices were subjected to HTSL testing for an extended period of time up to 2,016 h at 150°C and 175°C, and possible corrosion of Cu-Al IMC and copper wire are examined.

EXPERIMENTAL METHODS

Gaseous sulfur compounds were analyzed by the dynamic headspace concentration-gas chromatography-mass spectrometry (DHC-GC-MS) method. Cured mold compound powder was kept at four different temperatures (25°C, 150°C, 175°C, and 200°C), and headspace volatiles were collected on the trap for 10 min and analyzed by GC-MS.

Anions were determined by ion chromatographic (IC) analysis after the soluble components were extracted to water. Long-time application of high temperature and pressure brings hydrolyzable and soluble impurities such as halides into water [12, 13]. Finely powdered (particle size $\leq 10 \mu\text{m}$) cured mold compound (10 g) was agitated with 100 mL of ultrapure water for ~ 2 h in a Teflon cell. The homogenized solution was inserted into a sealed vessel, from Parr Instrument Company, that can withstand high temperature and pressure (maximum temperature: 250°C and pressure: 1,900 psi) and placed in an autoclave chamber at 121°C/100% relative humidity/2 atm for 24 h. After cooling, the solution was filtered into a clean Teflon container. This solution is referred to as “mold compound extract” (or simply “extract”). This extract was used for IC analysis.

Samples for HTSL were assembled in a 128-pin low-profile quad flat package) and encapsulated with mold compounds EMC-A and EMC-B. HTSL studies were conducted at 150°C and 200°C for various intervals of time up to 2,016 h. Every 500 h, samples were tested for any electrical failures and cross-sectioned by focused ion beam (FIB) and examined by scanning electron microscope (SEM) imaging for any corrosion.

RESULTS AND DISCUSSION

The National Institute of Standards and Technology best match compounds detected by DHC-GC-MS of sulfur-containing mold compound EMC-A at 25°C, 150°C, 175°C, and 200°C are shown in Table I and Fig. 1. As shown in Table I, no compounds were detected at 25°C. No sulfur-containing gaseous

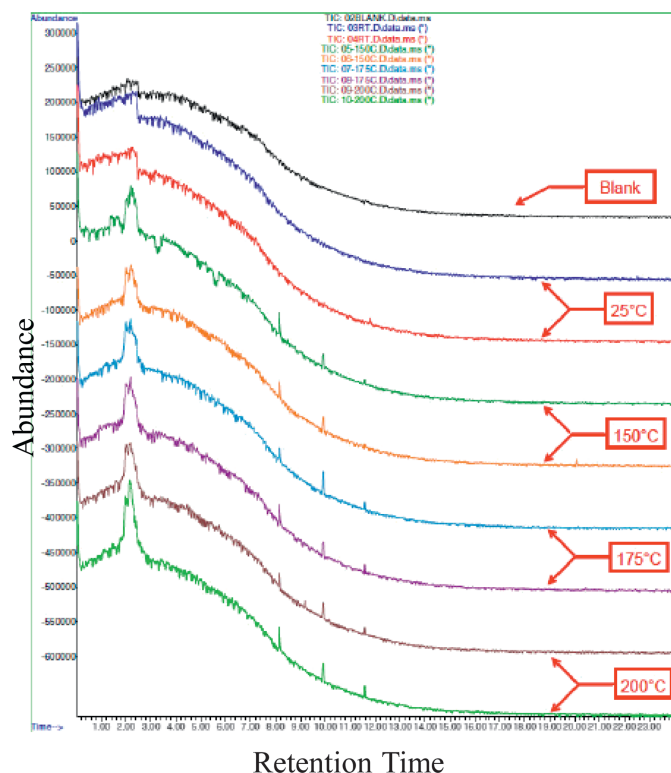


Fig. 1. DHC-GC-MS chromatograms of sulfur-containing mold compound EMC-A at different temperatures.

products were detected for the duration of the experiments indicating that no rapid decomposition of sulfur-containing adhesion promoter components occurred, even at a high temperature of 200°C, producing corrosive gases. Anionic species present in the mold compound matrix were determined by IC methods using mold compound extract. A comparison of chromatograms of aqueous standard solution containing sulfate, sulfite, and thiosulfate with mold compound extract is shown in Fig. 2. The only sulfur-containing anion detected in the mold compound extract was sulfate.

Ion chromatograms for standard aqueous solution of sulfide are compared with mold compound extract in Fig. 3. No sulfide was detected for the duplicate samples tested.

IC analyses showed that sulfate was the only sulfur-bearing anion in the mold extract samples (e.g., Fig. 2, Table II). It is quite possible that sulfite and sulfide could be oxidized to sulfate in presence of oxygen and high temperature when present in solution. Since mold compounds are insoluble in water and various ions need to be extracted to water with application of heat, determination of sulfate will provide a measure of total available sulfur-containing species present in the mold compound matrix.

High-temperature packaging reliability such as HTSL is typically tested at high temperatures, 150°C and 175°C, for 500-1,000 h and in some stringent reliability requirements even up to 2,000 h. Even though rapid decomposition of sulfur-containing adhesion promoter is not observed, it is not clear what happens when the mold compounds are subjected to extended thermal aging. If the decomposition of the sulfur compound is very slow, that amount of gaseous products are not

Table I
Compounds Detected by DHC-GC-MS of a Sulfur-Containing Mold Compound EMC-A, Heated to Various Temperatures

Detected compounds	Retention time	Relative abundance (10^5)			
		25°C	150°C	175°C	200°C
Hydroxyacetic acid, hydrazide	1.99	ND	55.4	58.2	80
Acetone	2.17	ND	93	103	171
Cyclotetrasiloxane, octamethyl	8.15	ND	9.4	11.8	12.3
Cyclopentasiloxane, decamethyl	9.9	ND	6.6	8.8	8.5
Cyclohexasiloxane, dodecamethyl-	11.58	ND	ND	2.8	4.2

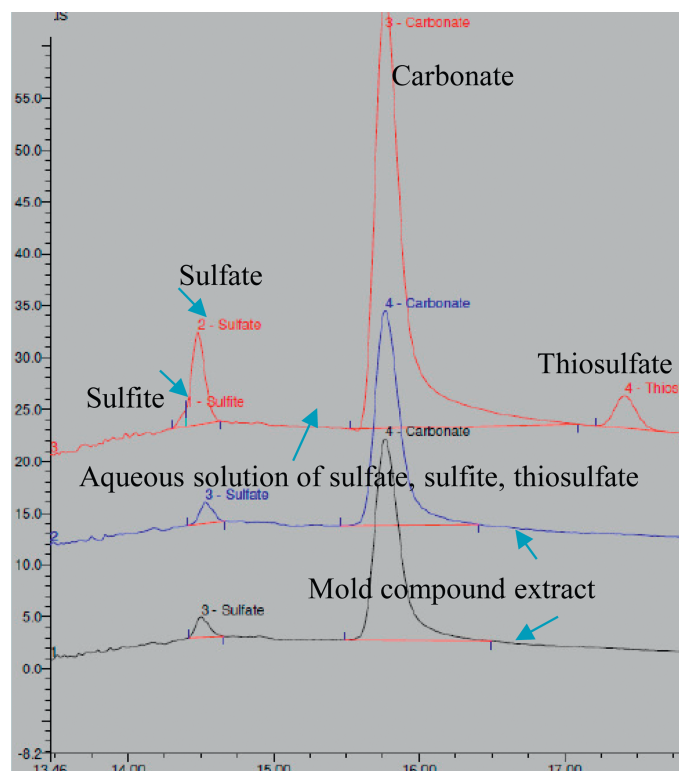


Fig. 2. ICs of aqueous standard solution containing sulfate, sulfite, and thiosulfate with mold compound (EMC-A) extract.

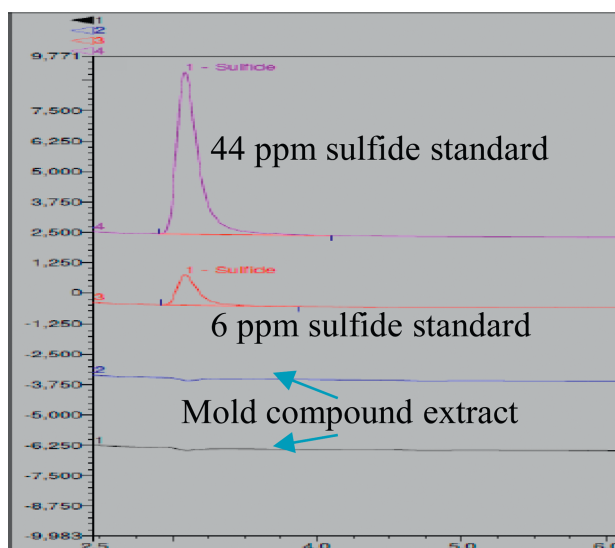


Fig. 3. IC comparison of aqueous sulfide standard and mold compound (EMC-A) extract.

enough to detect in short period of time, but in longer duration, e.g., 1,000 or 2,000 h, all of the sulfur compound could be decomposed. In such cases, the mold compound matrix may not contain any significant sulfur compound after 1,000 h of thermal aging. One way to test this possibility is to bake the cured mold compound powder for 1,000 h and 2,000 h and then conduct the aqueous extraction and analysis of the

Table II
Ionic Concentration of Mold Compound Matrix (EMC-A) after Thermal Treatment

	pH	Ionic concentration (ppm)					
		Na ⁺	NH ₄ ⁺	F ⁻	Cl ⁻	PO ₄ ²⁻	SO ₄ ²⁻
EMC-PMC	5.34	2.1	2	0.6	7.9	5.9	41.3
EMC-PMC + 175°C 1,000 h baking	5.15	2.4	2.1	1	32	5.6	44.3
PMC + 150°C 2,000 h baking	4.81	2.6	2.2	1.4	15.2	5.2	50.4

extract for sulfate. If all the sulfur compounds are completely decomposed with formation of gaseous products, IC analysis will result in zero, or a very small amount of sulfate compared with the initial sample. Table II shows the IC analysis results for ionic impurities after thermal aging in comparison with a post-mold cure (PMC) mold compound sample.

Sulfate levels were not found to be significantly changed for thermal aging of the mold compound at Automotive Electronics Council (AEC) Grade 0 condition of 1,000 h at 175°C, indicating that there is no sulfur compound decomposition or extremely slow decomposition without a significant amount of gaseous sulfur compounds produced. Aging for 2,000 h at 150°C (AEC Grade 0 condition) showed an increase in sulfate levels, indicating a small amount of decomposition of sulfur-bearing compounds. This degradation apparently did not result in offgassing of sulfur species, since this should have been reflected in lower sulfate levels with aqueous extraction. Comparing to the total amount of sulfur compound, level of decomposition is <1%. However, it may be noted that decomposition behavior of the adhesion promoter depends on the nature of the chemical components. Hence, decomposition rate can be different for different mold compound formulations.

The reliability impact of sulfur compounds on HTSL was tested on molded CuWB (bare Cu wire: 25 μm wire diameter) components after aging at 150°C and 175°C up to 2,016 h. Test units were encapsulated with two mold compounds: EMC-A (sulfate: ~40 ppm) and EMC-B (sulfate: ~45 ppm).

Electrical testing, including functional and open-short tests, after each read point showed no failures, confirming the integrity and reliability of CuWB packaging with these mold compounds, which contains substantial amounts of sulfur-containing compounds. Packaged samples were decapped (molding compounds were removed), and wire pull and ball shear tests were conducted to further evaluate the CuWB reliability. Fig. 4 shows the wire pull strengths after HTSL for the decapped samples. Wire pull strengths were found to be well above the specification level, and no degradation in pull strength was observed up to 2,016 h.

Fig. 5 shows corresponding ball shear strengths, which are above the specification for all durations. However, the EMC-A 2,016 h 175°C data spread appears to be larger due to the cracking of Cu-Al IMC (Fig. 6). This is not associated with sulfur compounds as indicated by absence of S or Cl in the energy-dispersive x-ray (EDX) analysis (not shown) of Cu-Al interface. Such isothermal aging degradation was also reported by other authors [14].

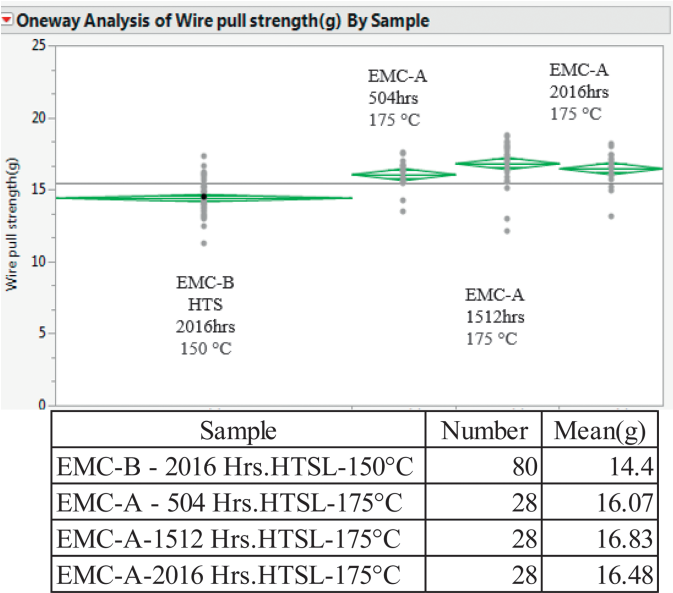


Fig. 4. Wire pull strengths after HTSL for CuWB dies encapsulated with sulfur-containing mold compounds.

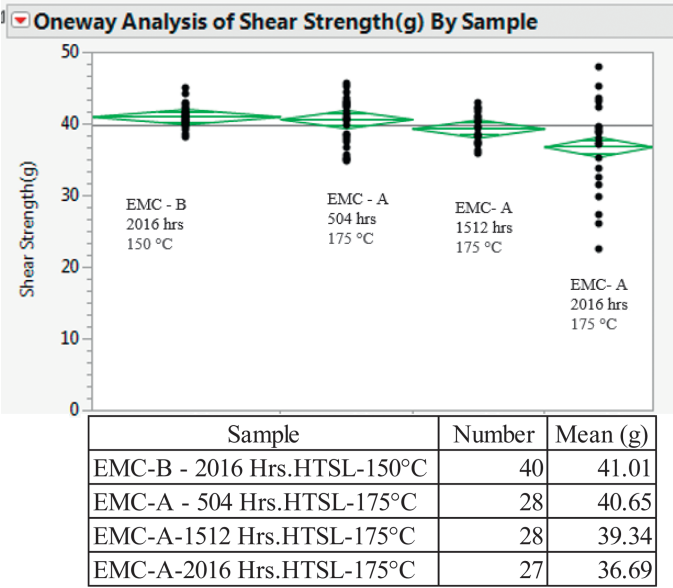


Fig. 5. Copper WB ball shear strengths after HTSL for CuWB dies encapsulated with sulfur-containing mold compounds.

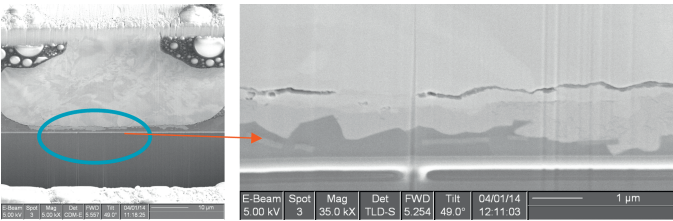


Fig. 6. FIB cross section of CuWB after 2,016 h of HTSL at 175°C showing Cu-Al interface IMC cracking.

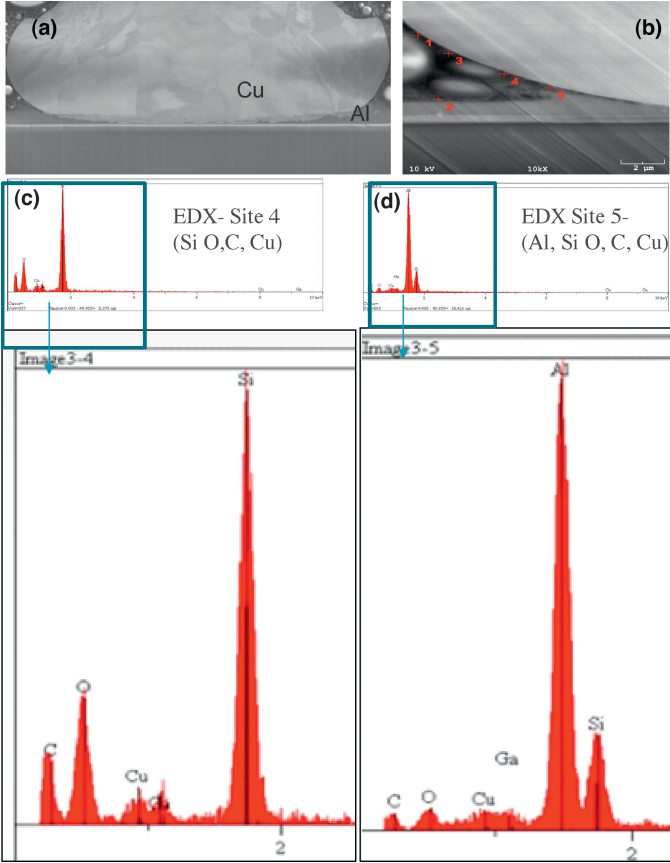


Fig. 7. FIB cross section of CuWB ball bond after 2,016 h of aging at 175°C for (a) CuWB ball bond, (b) Cu-Al interface, (c) EDX spectrum of site 4, and (d) EDX spectrum of site 5.

Fig. 7 shows SEM images of FIB cross sections of a copper ball bond (EMC-A) after 2,016 h of high-temperature storage (HTS) at 175°C. No Cu-Al IMC corrosion issues were observed at the Cu-Al interface. Extensive EDX spectroscopy analysis was carried out at various sites and no corrosive elements including S detected.

SEM images of FIB cross sections of the stitch bond after 2,016 h of HTS at 150°C are shown in Fig. 8. Very small amounts of copper corrosion at the Cu-mold compound interface were observed.

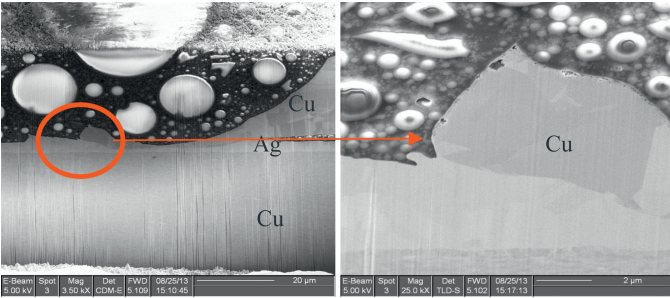


Fig. 8. FIB cross section of Cu stitch bond after 2,016 h of HTSL at 150°C showing minute Cu surface corrosion.

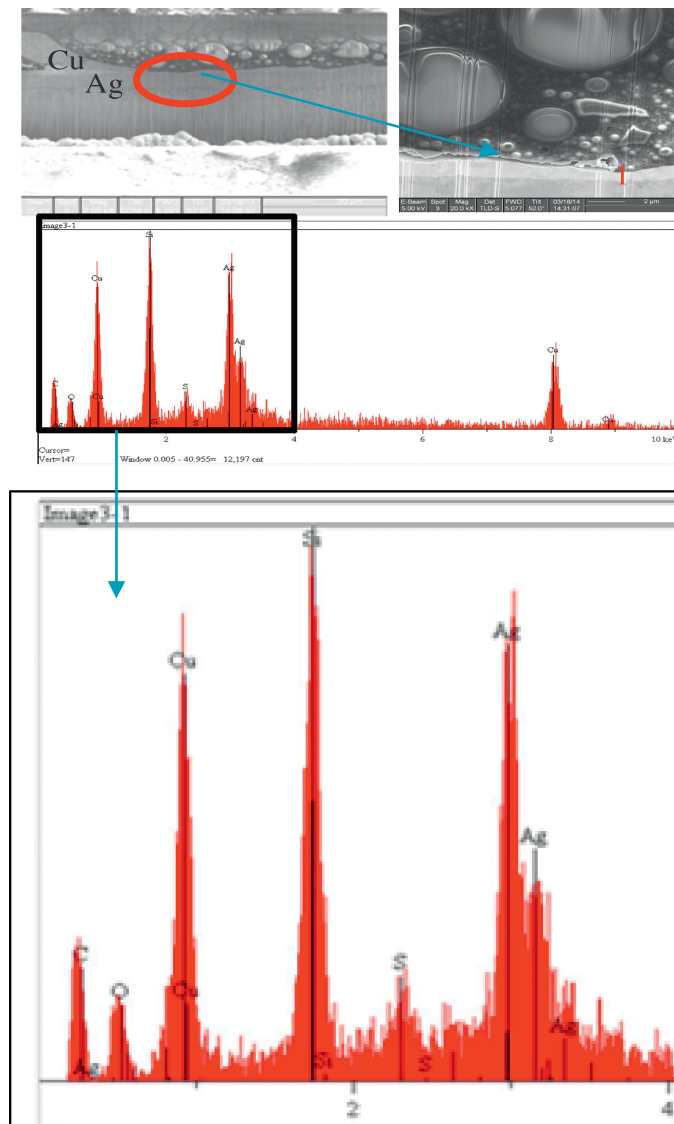


Fig. 9. FIB cross section of Cu stitch bond after 2,016 h of aging at 175°C with EDX spectrum of site 1.

As shown in Fig. 9, the level of corrosion is increased at 2,016 h of HTSL at 175°C. This level of corrosion is not significant enough to cause any electrical failures.

EDX spectrum (Fig. 9) shows the presence of S at the corroded area close to the Cu-mold compound interface, indicating the small level of corrosion is possibly caused by sulfur compounds. Sulfur-containing adhesion promoter components in the mold compound are expected to be enriched at this interface; hence, the presence of S or small level of corrosion under severe conditions is not unexpected.

CONCLUSIONS

Chromatographic analysis (DHC-GC-MS) at 150°C, 175°C and 200°C of mold compounds containing sulfur-based components did not show rapid evolution of gaseous sulfur compounds. Thermal aging studies at 150°C for 2,000 h and 175°C

for 1,000 h showed no significant formation of sulfur-containing gaseous compounds, but aging at these conditions appear to increase the level of aqueous-leachable sulfur compounds, measured as sulfate ion. HTSL reliability evaluation showed no reliability risk at HTSL-AEC Grade 0 conditions (175°C for 1,000 h or 150°C for 2,000 h). No sulfur was detected in the Cu-Al IMC bond interface. A small level of corrosion of Cu was observed in the end region of the stitch bond at the mold compound-Cu interface under a severe HTSL condition of 175°C for 2,016 h. However, this level of corrosion is not significant enough to cause any electrical failures. It may be noted that decomposition rates of sulfur-containing compounds depend on the chemical nature and concentration of specific compounds.

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