

Investigation of CuAl IMCs Corrosion in Chloride Environment and its Prevention Strategy

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Abstract

In most current wire-bonding applications, electrical interconnection is accomplished by fine Cu wires bonded to Al bonding pads microfabricated on an IC chip and external contact pins of the PCB board. Corrosion-related failure defects between the Cu wire and Al bond pad have been an ongoing un-trackable reliability issue plaguing the IC packaging industry for the past ten years, despite approaching ppb levels. Most prior studies hypothesized that intermetallic compounds (IMCs) like Cu_9Al_4 , and CuAl_2 were responsible for the observed acute wire-bond lift-off corrosion defects. Further studies sought to quantify the rates of corrosion of these IMCs and explore the effects of mitigation efforts of adding Pd, relevant to Pd-coated Cu wire-bonding. However, utilizing a novel real-time corrosion screening approach, we previously established that peripheral bimetallic contact between Cu ball-bonds and Al bond pads also plays a substantial role in the aggressive Al pad corrosion, induced by chloride ion penetration, which often leads to device failure. In this work, we further explored the role of IMCs corrosion in wire-bond lift-off failure utilizing fundamental electrochemical studies to quantify rates of galvanic-induced corrosion of IMCs within the broader context of an interconnected stack of Al bond pad, Cu-Al IMCs and Cu bonding wire. We also explored the use of a corrosion inhibitor to suppress the galvanic corrosion currents of Al bond pad, and Al-rich IMCs when electrically connected to Cu wire or Cu-rich IMCs.

Key words

Bonding failures, Cu-Al bonding interface, Cu-Al intermetallic compounds (IMCs), Cu wire-bonding, Galvanic corrosion

I. Introduction

Wire-bonding is one of the most commonly applied packaging technologies for IC fabrication and occupies a majority of IC packaging technology at about 75% despite the emergence of several advanced packaging methods such as flip chips [1]. Newer generations of flash memory and sensors also integrate wire-bonding in several forms [2]. And, there are IC packages that utilize both wire-bonding and 3-D stacking within the same device [3]. Wire-bonding technology is highly developed and relatively inexpensive; thus, its use is widespread. The use of copper (Cu) wire has steadily been on the rise, while gold and silver wires are commonly reserved for higher-end applications [4]. The advantages, growing market, and application potential of Cu wire-bonding were summarized by Zhong et al [5]. Cu is not

only less expensive than Au, but it also has lower resistivity, and higher thermal conductivity and mechanical strength. However, the drawbacks of Cu are its need for inert ambient protection and higher energy requirements for wire-bonding [6], [7], as well as its susceptibility to corrosion. Due to strict safety requirements, near-zero defects are required for the automotive microelectronics industry [8], which necessitates elimination of corrosion-related failures. Additionally, with the advent of wearable electronics, the ubiquitous halide and moisture contamination from consistent outdoor use introduces another need for preventing corrosion-related packaging failures [9].

One of the commonly reported wire-bonding failure modes in literature is the Cu ball bond liftoff due to corrosion

of the bonding region in mildly acidic chloride (Cl-) contaminated environments. Liftoff of Cu ball bonds was often observed after subjecting devices to highly accelerated stress test (HAST) under high temperature and humidity conditions [10]-[14]. Many reported mechanistic studies focused on the end result of corrosion after stress testing (including pressure cooker test (PCT), HAST, and biased HAST). The dominant mechanisms proposed in the literature [11]-[13] focused on Cu/Al intermetallic compounds (IMCs). Halide contamination, mainly from epoxy molding compounds (EMCs), was found to be one of the leading causes for corrosion at the ball bond interface [12], [13]. Applying a palladium (Pd) coating to the Cu wire was proposed and utilized as a solution for preventing this reliability issue as Pd could help to minimize IMC formation [11], [15]. Electrochemical characterizations of the IMC system at the Cu/Al ball bond interface, including galvanic corrosion testing were explored by [15], [16] on Al, Cu, and IMCs like CuAl_2 , and Cu_9Al_4 . The reports found the IMCs to be anodic with respect to Cu wire and cathodic with respect to the Al bond pad.

In our previous work, we established Cu-Al peripheral bimetallic contact between Cu bonding ball and Al bond pad can significantly contribute to the observed galvanic corrosion. Using a micro-pattern test platform, our results showed Al corrosion accelerated by Cu-Al bimetallic contact even without IMCs present [17]. Utilizing a real-time corrosion screening [18] we observed the corrosion of the Cu ball bond region, as well as the corrosion on Cu microdots on Al as it occurred. For the first time, hydrogen gas evolution was determined as an important factor for the Cu ball bond liftoff and subsequent wire-bonded device failure.

In this work, we sought to develop a broad mechanistic understanding of the multiple corrosion pathways that lead to the corrosion-induced liftoff of Cu/Al ball bonds and to utilize that in-depth understanding to develop more effective corrosion prevention strategies. In addition to the Cu-Al peripheral bimetallic contact we previously identified [17], there are also bimetallic contacts between Cu and IMCs, Al and IMCs, and even between the IMCs themselves [15], [16]. We considered the interface of the Cu-Al ball bond as depicted in Fig. 1, with Cu_9Al_4 and CuAl_2 as the major IMCs in between Cu and Al. As [19] points out, an encapsulated bonding device is likely only to have a thin electrolyte layer at the interface, meaning the complex stack of IMCs at the Cu-Al interface is more likely to behave as separate galvanic pairs instead of all being interconnected at once. Thus, the galvanic corrosion currents between Cu- Cu_9Al_4 , Cu_9Al_4 - CuAl_2 , and CuAl_2 -Al were measured separately. The possibility of Cu-Al galvanic corrosion due to the presence of Al bond splash, placing Cu and Al in direct peripheral

contact was discussed [17]. We explored the effect of adding a selected inhibitor *A* to the corrosion solution and observed that the corrosion rates of all galvanic pairs, and of the individual metals and IMCs dramatically decreased.

We also completed preliminary work on non-encapsulated Cu-Al wire-bonded devices utilizing a corrosion passivation coating that is compatible to packaging process flow. Initial corrosion immersion screening results indicated the coating provides 100% protection from Cu ball liftoff in extremely accelerated corrosion conditions, compared to the control devices which experienced over 85% wire-bond liftoff in as little as two hours.

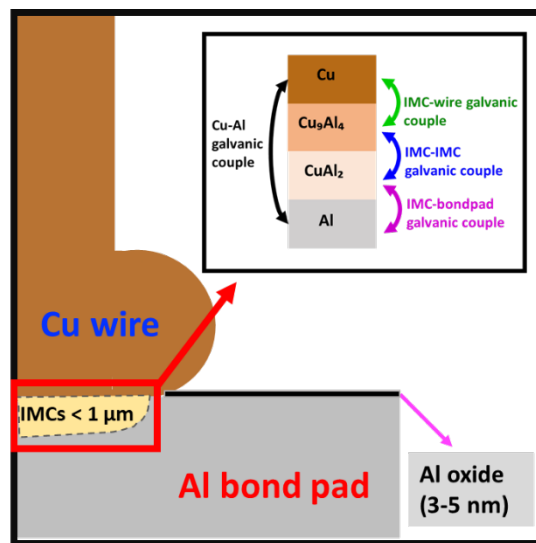


Fig. 1: Schematic of model Cu-Al ball bond interface. Inset shows major IMCs phases and locations with respect to Cu wire and Al pad.

II. Experimental

A. Electrode Preparation

Si wafers served as the substrate for the metals and alloys of interest, which were sputtered or plated. Pure Cu and Al alloyed with 0.5% Cu (in this work just referred to as Al) blanket wafers (~2um thick) were provided by NXP Semiconductors. The CuAl IMCs were sputtered on Si with a Ru barrier layer and Ti adhesion layer between the Ru and Si utilizing Denton Vacuum Desktop pro sputtering unit. The 99.99% pure Cu and Al targets from Kurt J. Lesker were used. After sputtering ~400 nm of IMCs, the IMC wafers were annealed at 400°C for 1 hour under 200 mTorr of nitrogen in Linberg/Blue Mini-Mite Tube Furnace. A Rigaku SmartLab X-Ray Diffractometer was used to carry out grazing angle XRD at 0.5° incident angle relative to the surface plane.

B. Potentiodynamic Polarization and Zero Resistance Ammetry

Electrochemical experiments were carried out on CH Instruments 440A. Potentiodynamic polarization (Tafel Plot) was conducted on a three-electrode system utilizing Pt counter electrode and Ag/AgCl in saturated KCl reference electrode. Scan rate used was 1 mV/s, and potential window was chosen to be approximately ± 0.2 V from stabilized OCP after 10 min of immersion in solution. Zero Resistance Ammetry (ZRA) was carried out as a two-electrode system in which the least noble metal/IMC was connected as the working electrode and the more noble metal/IMC was connected to reference and counter electrode leads of CH Instruments 440A potentiostat. In this setup, a positive current value indicates the WE is the anode, while a negative current indicates the CE is the anode. No potential or current was applied from the potentiostat in ZRA studies that measure direct galvanic current established between two electrically connected metal/IMC. Monitoring of galvanic current started immediately after immersion and was carried out for 12 hours. The measured current was divided by the surface areas of the electrodes to yield the current density. Solutions were prepared using 18.2 M Ω -cm ultrapure water from Millipore Sigma system, and ACS grade NaCl. Surface area of electrodes utilized in ZRA was ~ 0.50 cm², while surface area of WEs in potentiodynamic polarization was ~ 0.13 cm².

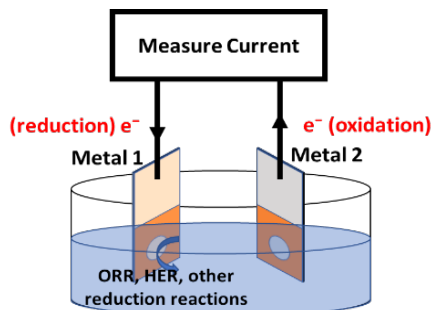


Fig. 2: Two-electrode configuration for Zero Resistance Ammetry measurements.

C. Cu-Al Wire-bonded Device Corrosion Immersion Screening and Coating Method

Non-encapsulated Cu-Al wire-bonded devices were obtained from NXP Semiconductors for use in corrosion immersion screening, details of which are previously published [17], [18]. Solution used for the corrosion immersion screening is the same 100 ppm Cl⁻ solution utilized in the electrochemical experiments in this work. Some wire bonded devices were subjected to a proprietary passivation coating [20]. Optical imaging of the corroding devices was collected using a Nikon LV150N metallurgical microscope with digital camera.

III. Results and Discussion

A. Grazing-Angle XRD of prepared IMCs

GR-XRD spectra of Cu₉Al₄ and CuAl₂ are provided in Figs. 3 and 4, respectively. The spectra were compared with reported work, and the major peaks were found to match IMCs prepared by an arc-melting method [16]. Like observed in [16], it is well known that some amount of Cu₉Al₄ is able to form within the CuAl₂ alloy (Fig. 4) [21].

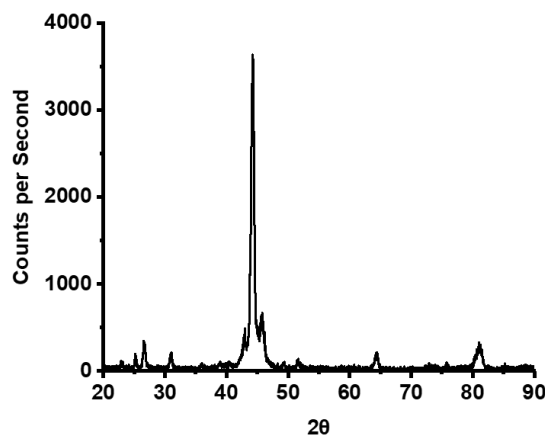


Fig. 3: Grazing angle XRD of Cu₉Al₄ sputtered on Si wafer. Major peaks match those as described by [16], indicating correct alloy phase formation.

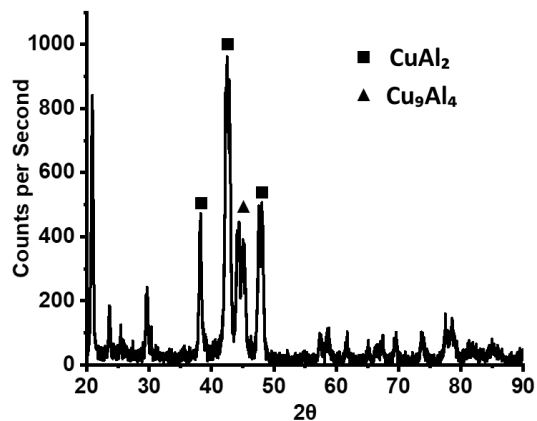


Fig. 4: Grazing angle XRD of CuAl₂ sputtered on Si wafer. Major peaks match those as described by [16] indicating correct alloy phase formation.

B. Galvanic Corrosion Behavior in 100ppm Cl^- and Influence of 0.1% wt/v Inhibitor

The galvanic corrosion currents of (Cu:Al), (Cu:Cu₉Al₄), (Cu₉Al₄:CuAl₂), and (CuAl₂:Al) plotted versus immersion time in 100 ppm Cl^- solution with and without 0.1% wt/v inhibitor *A* are shown in Fig. 5, 6, 7, and 8. The corrosion current values remained positive throughout the entire 12 hrs, indicating Al was the anode of the Cu:Al and CuAl₂:Al couples, Cu₉Al₄ was the anode of the Cu:Cu₉Al₄ couple, and that CuAl₂ was the anode of the Cu₉Al₄:CuAl₂ couple. The average corrosion current densities are visualized in Fig. 9 (averages were used since not all experiments yielded stable current).

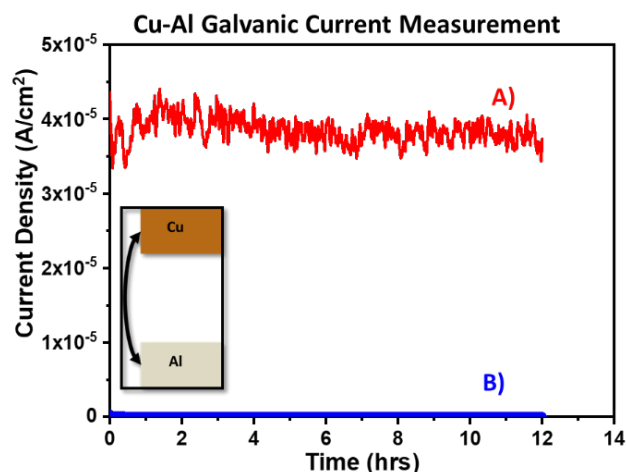


Fig. 5: ZRA plot of current density as a function of time for Cu:Al galvanic couple with immersion in 100 ppm Cl^- solution. A) without inhibitor and B) with 0.1% (w/v) inhibitor in solution.

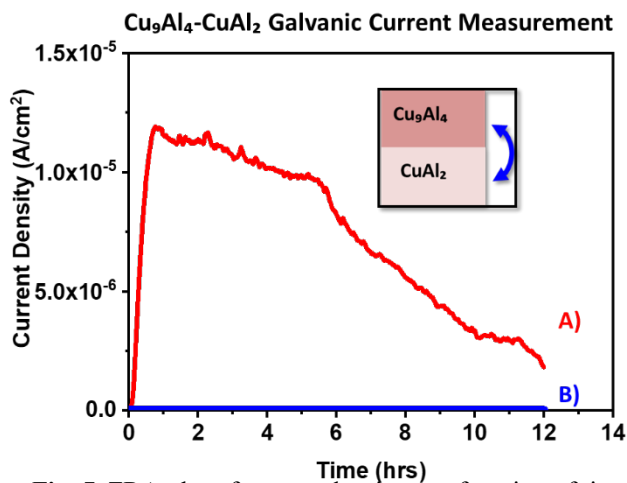


Fig. 7: ZRA plot of current density as a function of time for Cu₉Al₄:CuAl₂ galvanic couple with immersion in 100 ppm Cl^- solution. A) without inhibitor and B) with 0.1% (w/v) inhibitor in solution.

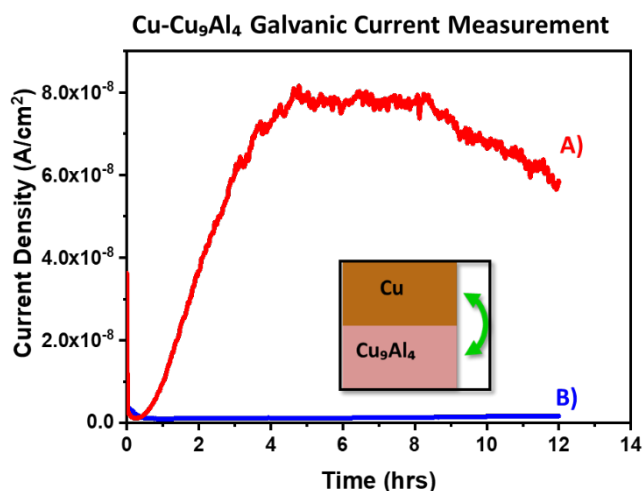


Fig. 6: ZRA plot of current density as a function of time for Cu:Cu₉Al₄ galvanic couple with immersion in 100 ppm Cl^- solution. A) without inhibitor and B) with 0.1% (w/v) inhibitor in solution.

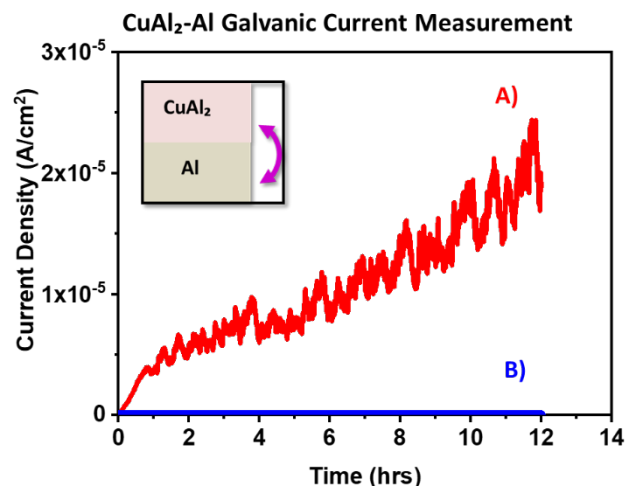


Fig. 8: ZRA plot of current density as a function of time for CuAl₂:Al galvanic couple with immersion in 100 ppm Cl^- solution. A) without inhibitor and B) with 0.1% (w/v) inhibitor in solution.

While we found the average galvanic corrosion rate of $\text{CuAl}_2:\text{Al}$ to be slightly faster than $\text{Cu}_9\text{Al}_4:\text{CuAl}_2$, the initial corrosion rate of $\text{Cu}_9\text{Al}_4:\text{CuAl}_2$ was actually faster for the first five hours of corrosion. We hypothesize the decrease in $\text{Cu}_9\text{Al}_4:\text{CuAl}_2$ corrosion current density, as well as the steady increase in corrosion current density in $\text{CuAl}_2:\text{Al}$ could be attributed to the de-alloying of CuAl_2 into Cu or more Cu-rich IMCs due to localized pitting corrosion and selective micro-corrosion of the less noble Al within CuAl_2 [22], [23] because chloride is well known for breaking down the normally protective Al oxides [24]-[26]. As the CuAl_2 de-alloys into Cu, that electrode takes on a stronger cathodic character, thus resulting in decreasing current when connected to pure Cu, and increasing current when connected to Al.

While it is common in post-mortem analyses to observe the disappearance of Cu_9Al_4 after wire-bond liftoff, our data does not support that the Cu_9Al_4 is the ‘weak link’ at the Cu ball bond interface [27]-[29]. As [19] hypothesized, it seems the disconnect is more likely to propagate elsewhere, like at the $\text{Cu}_9\text{Al}_4\text{-CuAl}_2$ interface due to their much higher galvanic corrosion current compared to $\text{Cu}:\text{Cu}_9\text{Al}_4$. It is only after wire-bond liftoff that the initially small amount of Cu_9Al_4 corrodes away due to its galvanic-driven corrosion through its connection with Cu.

It was observed in all cases that addition of 0.1% wt/v of inhibitor *A* drastically reduced galvanic corrosion by several orders of magnitude, demonstrating the effectiveness of inhibitor *A* to not only suppress the corrosion in the Cu:Al galvanic system as we previously reported [17] but also the galvanic corrosion of the IMCs and the IMC’s self-corrosion. It should also be noted that direct submersion of these electrodes in 100 ppm chloride is an extreme condition that the ball bond region would not normally be subjected to in an encapsulated device, thus highlighting the corrosion protection potential of inhibitor *A*. Practical application of targeted passivation coating is currently in development for

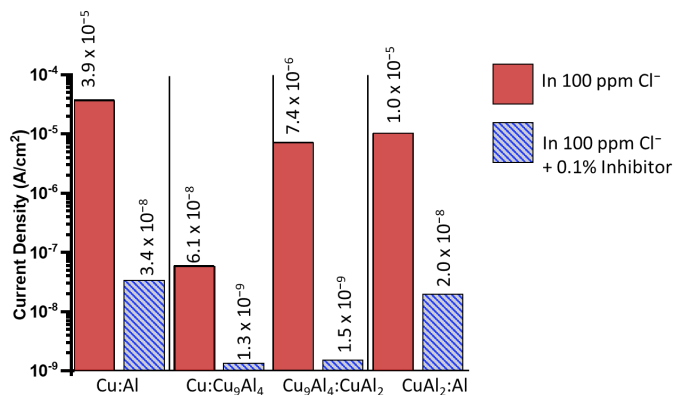


Fig. 9: The average current density values of galvanic corrosion currents during 12 hour immersion in chloride and chloride + inhibitor solutions.

wire-bonded devices, with preliminary corrosion immersion screening results of coated devices contained herein.

C. Individual Corrosion Behaviors in 100ppm Cl^- and Influence of 0.1% wt/v Inhibitor

Potentiodynamic polarization and Tafel plot analysis was carried out to understand the corrosion protection effects of inhibitor *A* on the individual metals and IMCs in chloride environment. Fig. 10 is a consolidated graph of the resulting Tafel plots. As seen in Fig. 10 and Table 1, addition of 0.1% inhibitor significantly decreases the individual corrosion rates of each metal and IMC. However, only Cu’s E_{corr} is shifted to a more positive potential after addition of the inhibitor, while the E_{corr} s of Al and Al-containing alloys shifted to more negative potentials. In our previous work, we identified inhibitor *A*’s mechanism of suppressing bimetallic corrosion in the Cu:Al system to act on the cathodic hydrogen evolution reaction on Cu surface [17]. We hypothesize the reason for the opposing changes in E_{corr} to arise from the inhibitor’s preferable interaction with Cu. Thus, in the CuAl IMCs, the electrochemical behavior of Cu is suppressed due to some passivation provided by the inhibitor, allowing the Al to dominate the electrochemical behavior and shift the E_{corr} to more negative potentials.

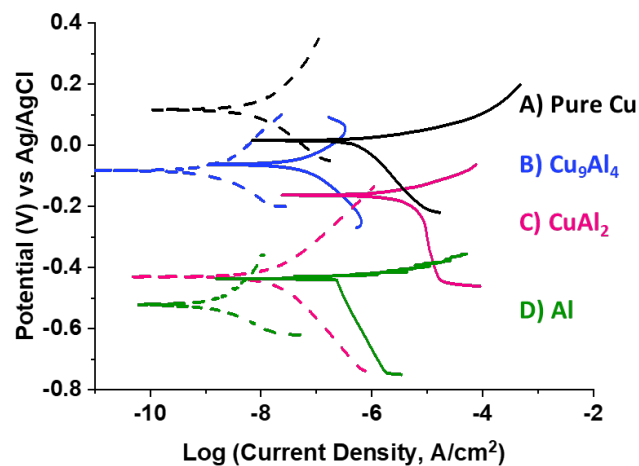


Fig. 10: Tafel plots of the metals and alloys utilized in this study in 100 ppm Cl^- (solid lines) and 100 ppm Cl^- + 0.1% inhibitor (dotted lines) for A) Pure Cu, B) Cu_9Al_4 , C) CuAl_2 , and D) Al.

D. Corrosion Immersion Screening of Cu-Al Wirebonded Devices

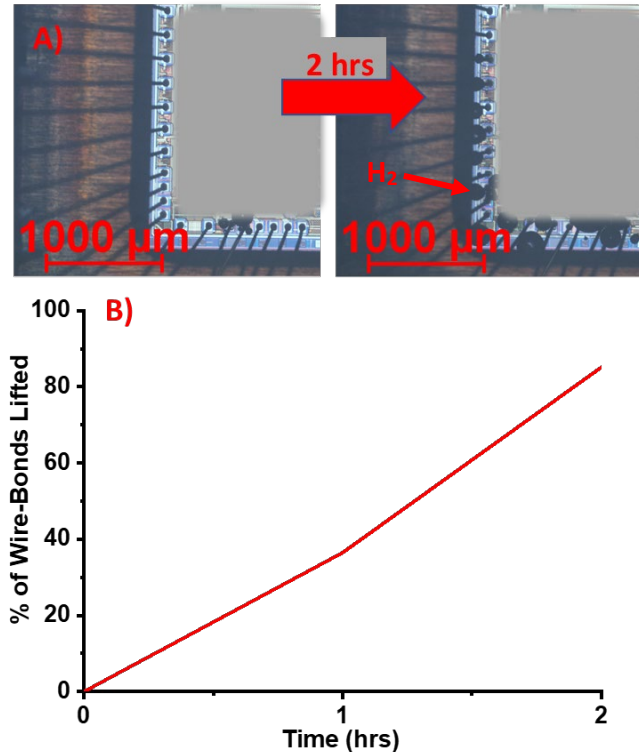


Fig. 11: Corrosion immersion screening of uncoated Cu-Al wire-bonded device in 100 ppm Cl⁻. A) Optical microscopy images at initial and after 2 hrs immersion and B) plot of percentage of wire-bonds lifted off with respect to immersion time.

Fig. 11 and 12 illustrate the corrosion protection afforded by the selected passivation coating applied to a Cu wire-bonded device. The corrosion immersion screening the devices are subjected to is an extremely harsh condition, 100 ppm Cl⁻ aqueous solution, and drastically worse than what a device would be subjected to in normal operation. This extreme condition is intended to accelerate the corrosion process to be observable within a timeframe of hours. The un-modified device with no coating (Fig. 11) experiences over 85% liftoff within two hours of immersion. It is worth noting that hydrogen evolution was clearly seen during the active corrosion leading to Cu ball lift-off. In contrast, the device with passivation coating (Fig. 12) experiences no wire-bond liftoff or Al pad corrosion within the same timeframe.

As observed in our previous work [17] the in-situ monitoring of the uncoated device revealed corrosion initiated at the Cu/Al ball bond interface with active Al_xO_x dendrite formation and H₂ gas evolution. The corrosion was observed to expand around the perimeter of the Cu ball and the remaining Al pad, leaving the “mud-crack”

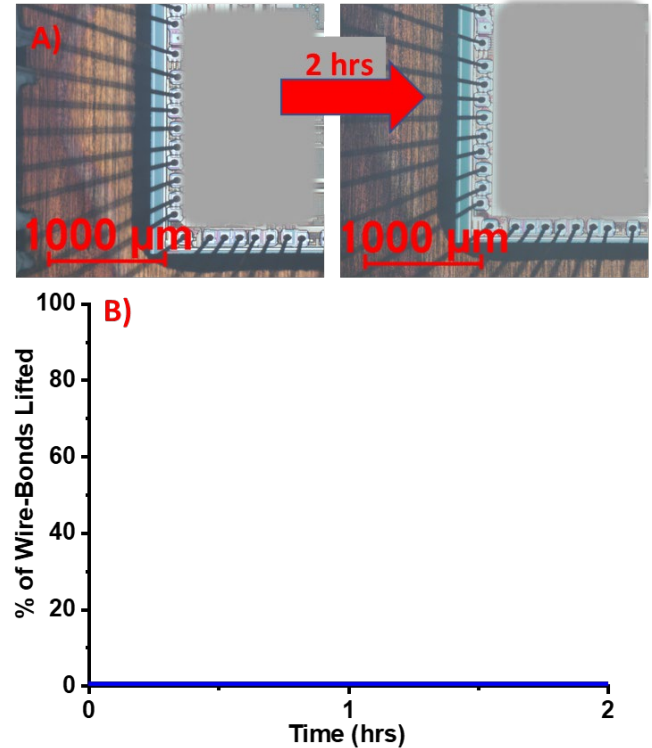


Fig. 12: Corrosion immersion screening of Cu-Al wire-bonded device with Inhibitor A coating in 100 ppm Cl⁻. A) Optical microscopy images at initial and after 2 hrs immersion and B) plot of percentage of wire-bonds lifted off with respect to immersion time.

morphology. The corrosion then proceeded under the Cu ball bond to attack the underlying Al and/or CuAl IMCs that were previously concealed. Only after this final step was the Cu ball observed to liftoff [17].

The coated devices, tested under identical conditions as the uncoated devices, did not exhibit Al pad corrosion, nor the accompanying H₂ evolution. This result indicates the selected passivation coating is able to block one of the key enablers of the galvanic-induced corrosion of the Cu/Al ball bond region, the cathodic hydrogen evolution reaction [17]. This result, combined with the ZRA and Tafel plot experiments on the CuAl IMCs, indicates the passivation coating shows potential to provide broad-spectrum protection over the various interfacial corrosion pathways involving the individual IMC's corrosion, and the galvanic corrosion between (Cu:Al), (Cu:Cu₉Al₄), (Cu₉Al₄:CuAl₂), and (CuAl₂:Al) that can lead to the Cu ball liftoff and device failure. Continued fundamental corrosion studies of the effect of passivation coating directly on the IMCs themselves is currently on-going to better understand the inhibition mechanism for these systems.

Table 1: Consolidated Tafel plot calculations for metals and IMCs in 100 ppm chloride with and without 0.1% inhibitor.

Sample	Polarization Resistance (Ω)	Corrosion Current Density (A/cm^2)	Corrosion Rate (Angs/min)	Corrosion Potential (V vs Ag/AgCl)
Cu in 100 ppm Cl^-	1.2×10^5	1.03×10^{-6}	0.22000	0.02
Cu in 100 ppm Cl^- + 0.1% inh.	2.6×10^7	1.03×10^{-8}	0.00230	0.115
Cu_9Al_4 in 100 ppm Cl^-	2.8×10^6	8.75×10^{-8}	0.01900	-0.06
Cu_9Al_4 in 100 ppm Cl^- + 0.1% inh.	1.3×10^8	1.99×10^{-9}	0.00040	-0.08
$CuAl_2$ in 100 ppm Cl^-	4.7×10^4	3.26×10^{-6}	0.79000	-0.16
$CuAl_2$ in 100 ppm Cl^- + 0.1% inh.	1.4×10^7	1.91×10^{-8}	0.00460	-0.43
Al in 100 ppm Cl^-	2.7×10^5	4.93×10^{-7}	0.10000	-0.43
Al in 100 ppm Cl^- + 0.1% inh.	9.4×10^7	2.15×10^{-9}	0.00045	-0.52

IV. Conclusions

The various galvanic corrosion cells at the Cu ball bond interface were individually explored by the ZRA technique. It was found that galvanic corrosion rates followed as such: Cu:Al > $CuAl_2$:Al > Cu_9Al_4 : $CuAl_2$ >> Cu: Cu_9Al_4 , with Cu_9Al_4 : $CuAl_2$ corroding faster than $CuAl_2$:Al for the first five hours of corrosion. The ZRA data supports previous work that identifies the Cu_9Al_4 : $CuAl_2$ interface, not Cu_9Al_4 itself, is a likely culprit for observed wire-bond liftoff. The data also supports the case of peripheral bimetallic Cu-Al contact, when IMCs are hidden, is a potential corrosion pathway for eventual ball bond liftoff. Inhibitor A, simply added to the corrosion solution, is able to suppress corrosion in all the galvanic cells studied, and even on the individual metals and IMCs themselves. A targeted passivation coating application, currently in development, shows promise in eliminating the corrosion-induced liftoff failure of Cu ball bonds, increasing the longevity and reliability of devices utilized in high-stress, moisture, heat, and humidity applications. Further work on understanding the mechanism of protection afforded by a targeted passivation is underway. However, preliminary corrosion immersion screening of non-encapsulated Cu-Al wire-bonded devices indicates the selected passivation coating can protect the Cu ball bond from liftoff despite the presence of multiple corrosion pathways that could lead to device failure.

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