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The critical oxide thickness for Pb-free reflow soldering on Cu substrate

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ABSTRACT

Oxidation is an undesirable effect of reflow soldering. Non-wetting occurs when the oxide layer grows above the critical thickness. Characterizing the critical oxide thickness for soldering is challenging due to oxide's nano-scale thickness and irregular topographic surface. In this paper, the critical copper oxide thickness was characterized by Time-of-Flight Secondary Ion Mass Spectrometry, Scanning Electron Microscopy, Energy-Dispersive X-ray spectroscopy, and Transmission Electron Microscopy. Copper substrates were coated with an Organic-Solderable-Preservative (OSP) layer and baked at 150 °C and 85% Relative Humidity for different amounts of time. The onset of the non-wetting phenomenon occurred when the oxide thickness reached 18 ± 5 nm. As the oxide grew beyond this critical thickness, the percentage of non-wetting solder joint increased exponentially. The growth of the oxide thickness followed a parabolic rate law. The rate constant of oxidation was 0.6×10^{-15} cm^2 min^{-1}. Oxidation resulted from interdiffusion of copper and oxygen atoms through the OSP and oxide layers. The oxidation mechanism will be presented and discussed.

1. Introduction

Solder joint formation requires an oxide-free surface to bond between the substrate pads and solder ball during soldering [1]. The common solderable materials in Pb-free solder are Sn, Cu, Ag, Zn, Bi, In, and Sb [2,3]. Other electronic materials such as Au, Co, Pt, Pd, Fe, and Al are occasionally introduced to the solder for alloying effects [3]. For the substrate, there is always a solderable protective layer coated on top of the Cu. This surface finish can either be the Electrolytic Nickel-Gold, Electroless Nickel-Gold, Immersion Tin, Immersion Silver, Electroless Nickel-Electroless Palladium-Immersion Gold, Hot Air Solderable Leveling, Solder on Pad, or Cu Organic-Solderable-Preservative (OSP) [4,5]. However, during or after coating the protective layer, a thin and stable native oxide layer is rapidly formed [6,7]. In general, the native oxide's thickness ranges from 2 to 10 nm [7–9]. Theoretically, this thin oxide layer acts as a diffusion barrier to prevent further oxidation, and a parabolic growth law is normally observed [6,7,10–13]. However, the theory assumes a perfectly uniform oxide layer [6,10,13] while most naturally-grown oxide contains structural defects [7,14,15]. These defects short-circuit the diffusion path [16] and permit further diffusion. An actual oxide thicker than theoretical expectations [8,12] then results. When the oxide grows too thick, the organic flux that is introduced to the soldering process may not remove the oxide completely, and a non-wetting solder joint is formed. The electrical interconnection will then fail prematurely [2]. For years, the electronic assembly industries have been searching for the critical oxide thickness that will trigger non-wetting. This allows them to effectively control the oxide thickness for the soldering process. However, there is a lack of widely accepted published data, mainly because analyzing the irregular nano-scale oxide layer requires meticulous work. Thus, most studies have focused on wettability [2,17,18]. Therefore, it is of interest to characterize the critical oxide thickness for non-wetting reaction during reflow soldering.

In this work, the oxidation of Cu-OSP is chosen. This surface finish offers several advantages in terms of cost, surface flatness, and reliable solder joint [19,20]. In addition, Cu has been applied to the metallization layer in electronic devices due to its high thermal conductivity and resistance to electron-migration [14,15,21,22]. The Cu oxidation processes from initiation to thick oxide film have been comprehensively researched over 50 years [7,10–15,19–28]. Therefore, good reference data can be employed for comparison. Table 1 is the kinetics data published [19,21–28] for Cu oxidation from 100 °C to 175 °C. In this low temperature regime, Cu_2O is formed [19–23,29–32]. Wijk et al. [33] reported that the variation of oxidation energy is small and only 4.8 kJ mol^{-1}. However, Table 1 shows a considerable scatter of the activation energies ranging from 32.8 kJ mol^{-1} to 166.9 kJ mol^{-1}, and the rate constants are at 10^{-16} to 10^{-15} cm^2 min^{-1}. These studies were done either based on weight gain, contact sheet resistance, sputtering, or polarizing spectrometer. For Cu-OSP, Ramirez et al. [19] calculated the rate constant of oxidation as 1.92×10^{-13} cm^2 min^{-1}, which is high compared to direct Cu oxidation in Table 1. Ramirez's result contradicts

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Table 1
Kinetics data from literature for oxidation of Cu at 100 °C to 175 °C and thickness of the oxide ranges from 10 to 600 nm [19,21–28].

Oxidation Conditions	D (cm^2/s)	E (kJ/mol)	Diffusion limited regime (nm)	Mechanism	Reference
Poly-crystal Cu 99.95% at 150 °C at clean air	0.6×10^{-15}	166.9	1–278	Parabolic	Pinnel et al. [23]
Sputtered Cu at 140 °C ambient air	0.52×10^{-15} 3.2×10^{-15}	55.0	5–25	>16 nm parabolic <14 nm inverse logarithmic	Zhong et al. [21,22]
Poly-crystal Cu at 155 °C and air reflow	1.92×10^{-13}	32.8	4–42	Parabolic	Ramirez et al. [19]
Bulk, sputter, electroless Cu 99.9% at 100 °C and dry air		71.4	5.5–7.5	Inverse logarithmic	Reilly et al. [26]
Sputtered Cu at 175 °C and dry air	5.44×10^{-15}	31.8	3–11	Linear rate	Njeh et al. [27]
Electroplated Cu at 150 °C on Co hardened Au	1.29×10^{-13}	75.3	1.7–46	Parabolic	Tompkin and Pinnel [24,25]
	3.47×10^{-26}	199.7		Lattice self diffusion	Tu et al. [28]

the idea that the OSP layer is supposed to behave as a protective layer from oxidation. Besides, it is noteworthy that the conjectured oxidation mechanisms at this low temperature differ amongst the authors. Clearly, the direct correlation between the oxide thickness and detailed structure of the layer is not completely explained, particularly in Cu-OSP.

This paper focuses on the oxidation of Cu-OSP from the thin to thick film stage. The objective is to determine the critical oxide thickness of a copper substrate for soldering, thereby providing referenced oxide data for the assembly process and a different approach to measure oxide thickness directly. The kinetics of oxidation processes, mechanism of oxide growth, and surface topographical evolutions will be presented.

2. Experimental procedures

Ball Grid Array substrates were used in this study. Sampled substrates consisted of 225 copper pads with 0.3 mm pad diameter and 0.35 mm pad pitch. Copper pads were electro-chemically plated with a purity of 99.9% weight of copper. These pads were coated with a 100 nm commercial imidazole layer (Entek® Plus Cu-106A supplied by Tamura Kaken Co. Ltd. Japan) as an OSP. The Cu substrate was first cleaned by ethanol, followed by micro etch using 5% sulfuric acid (H_2SO_4) to enhance the surface roughness for OSP coating. After micro-etch, the substrates were rinsed by water and dipped into Entek Plus Cu-106A bath. The OSP coated substrates were then rinsed with distilled water and dried.

The OSP coated substrates were then baked at 150 °C and 85% relative humidity (RH) for 168 h. Every 12 h, a few of substrates were taken out for surface analysis. Oxide depth profile was performed by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) with a low energy Bi primary beam of 25 kV. Substrates were sputtered with Cs^+ ion at 193 kJ mol^{-1} energy and 1.3×10^{-4} Pa vacuum level. The specimens were tilted at 30° angle and scanned for an estimated 70 μm^2 area. The sputtering rate was approximately 2.2 nm per 20 s, calibrated by using a silica sample [34]. Sputtering time was set at 880 s. The secondary ion cluster CsX^- was then analyzed. Bright Field Transmission Electron Microscopy (BF-TEM, JEOL JEM-2100 F) was used to correlate to the estimated oxide thickness based on the sputtering rate.

The different pre-baked Cu-OSP substrates were printed with a water-soluble flux. Sn3.5Ag0.5Cu solder balls with 0.3 mm diameter were placed on the Cu pads. Soldered substrates were then reflowed at peak temperature of 245 °C; with time above liquidus of 60 s and the ambient oven was controlled below 20 O_2 ppm. Upon solidification, the solder balls were sheared off using Dage-4000. Fracture interfaces of the solder joint were checked as to verify the non-wetting mode. The percentage of non-wetting solder joint was then calculated. For the onset of non-wetting solder joint, the pre-baked bare Cu-OSP substrates were analyzed using Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi S-4800) at an operating voltage of 15 kV for secondary micrographs. This FE-SEM was equipped with Energy-Dispersive X-ray spectroscopy (EDX), and the elemental mapping was performed at 5 kV using EDX. Thickness and surface topography of oxide were further studied in details by using TEM operated at 200 kV. The surface roughness (R_a) was then measured using Wyko NT9100.

For TEM sample preparation, a layer of silica was coated to the specimen to protect the oxide layer using direct-write chemical vapor deposition (CVD) technique [35]. Oxygen and siloxane (Tetramethylcyclotetrasiloxane, $Si_4O_4C_4H_{16}$) were used as chemical precursors and guided to a small region for TEM analysis. A Focused Ion Beam (FIB) of Ga^+ ion with 50 kV was introduced to provide the necessary energy for CVD. While silicon oxide was deposited onto a small area, its thickness was inspected in-situ by

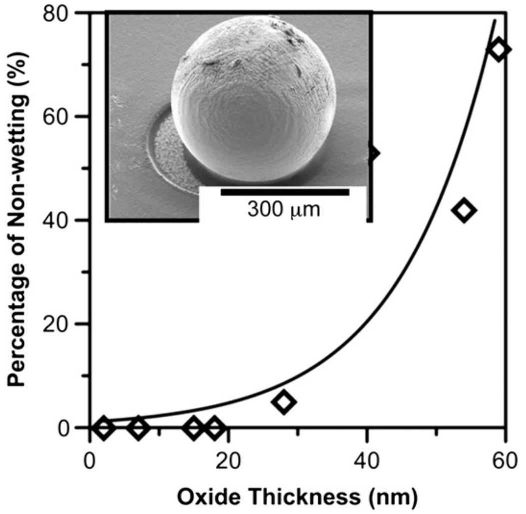

Fig. 1. Effects of Cu oxide thickness on percentage of non-wetting solder joint.

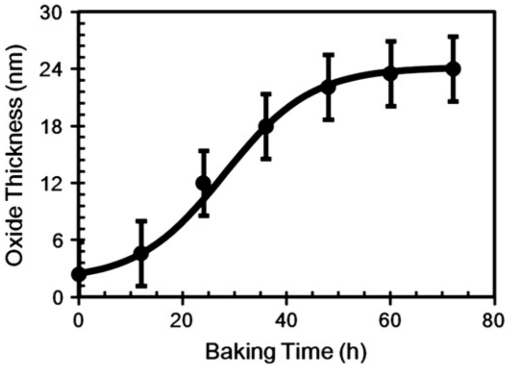

Fig. 2. Effects of baking hour on the thickness of Cu_2O at 150 °C and 85% RH.