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Rapid method for testing efficacy of nano-engineered coatings for mitigating tin whisker growth

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ABSTRACT

The risk of failure of electronic components due to tin (Sn) whiskers growth has become an issue with the current regulations limiting the use of lead in Sn solders. New strategies using engineered coatings for mitigating Sn whiskers are being developed. Typically, these coatings are evaluated by an aging process where whiskers are allowed to grow naturally. Unfortunately, this process can produce unreliable growth results and can take several years. Thus, faster, more reliable methods are needed. In this study, a simple, rapid (3–10 days), and cost-effective method was developed for testing the efficacy of nano-engineered coatings for mitigating the growth of Sn whiskers. This method consisted of a micro-indentation process using a ball-bearing adhered to a few hundred gram weight, which are placed in a stabilizing printed holder. For uncoated samples, Sn whiskers and hillocks were abundant near the indentation area, while only hillocks were found further outside the area (i.e., >0.2 mm). For samples coated with nano-engineered ceramic or polymeric coatings, the indentation method was observed to damage coatings only at the point of contact (e.g., no delamination), while still allowing Sn whiskers and hillocks to grow outside the indentation area.

1. Introduction

The drive for lead-free electronics has increased interest in using pure electroplated tin (Sn) in electronic components. While Sn platings do not pose a health threat, they suffer from spontaneous formation of single crystal whiskers that can reach lengths of several millimeters and cause short-circuiting of electrical components [1,2]. The risk of failure due to Sn whiskers has driven interest in understanding the fundamentals of their formation and developing coatings that mitigate their growth [3].

One source for the growth of Sn whiskers and hillocks (a Sn hill-like protrusion) is thought to be caused by compressive stresses arising from either internal (e.g., intermetallic compound diffusion) or external (e.g., bending) loads [4]. Internal stresses arise at the copper (Cu) substrate and Sn plating interface due to formation and diffusion of intermetallic compounds (IMC) such as Cu_6Sn_5. This leads to an increase in compressive forces that initiates growth of whiskers along the columnar grain interfaces [5,6]. Internal stresses in the Sn plating can also arise from formation of Sn oxide films (e.g., SnO, SnO_2) after the Sn surface is exposed to air or moisture [6,7]. This mechanism is likely responsible for increased whisker growth in humid conditions [7].

A variety of coatings including urethane, epoxy, Parylene C, silicone, and acrylic have been proposed for mitigation of Sn whisker growth [3,8,9]. The efficacy of particular coatings is dependent on their thickness, mechanical properties, surface energy, and, in some cases, testing conditions [8]. In general, a thicker coating is more likely to prevent whisker growth. However, thicknesses higher than ~50 to 400 μm may create excessive stresses on the electronic components (e.g., solder joints) [10]. This aspect is exacerbated by use of rigid coatings such as epoxy and some urethanes [10]. Conversely, for films applied using either spray or dip coating, a minimum thickness of about 10–50 μm is needed to ensure their continuity [10]. A likely location for whiskers to cause a problem is in connectors, which is also where coatings can be an issue if they are too thick such that connector efficiency is lost [4]. Significantly thinner conformal coatings can be fabricated using vapor deposition methods. However, thus far only relatively thick (~20 μm) Parylene C films grown by catalytic vapor deposition (CVD) have been tested for whisker mitigation.

Evaluation of the efficacy of coatings is difficult because of the slow and unpredictable nature of the Sn whisker growth. The most common testing method is aging of Sn plated Cu samples under

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ambient or humid conditions and relying on the natural IMC-induced stresses to drive whisker formation. Unfortunately, this process occurs on very long time scales (sometimes as long as a year) and can often result in inconsistent whisker growth. To speed up the evaluation period, a variety of external methods have been developed for generating internal stresses at a faster rate. These include thermally and mechanically (e.g., bending, scratching, indentation) induced stresses. One approach to inducing thermal stresses is to thermally cycle Sn-plated samples [11]. This method consists of rapid sample cooling and heating cycles that induce compressive and tensile stresses, respectively. While effective, the rapidly grown whisker population using this method is not necessarily representative of that found on naturally aged samples [11]. In addition, for coatings with a thermal expansion coefficient that mismatches with the Sn plating, thermal cycling could lead to coating delamination. Since this may not occur under normal operating conditions, non-representative results on the coating efficacy could be obtained. Routes to mechanically induce stresses include bending [12], scratching [8], pressing [13], and indentation [4,14–21]. The latter approach has been successfully used to accelerate whisker growth using both nanoscale [14–18] and microscale [4,19–21] indenters. Nano-indentation generates very localized compressive stresses; however, this only leads to growth of a single whisker from the nanoscale indented region. While this approach is quite attractive for *in-situ* studies of the whisker growth mechanisms, it is not optimal for evaluating coatings because the nano-indenter must break through the coating to apply direct stress to the Sn plating. In this region, the coating is removed or damaged and proper evaluation of its efficacy for stopping whisker growth cannot be achieved. Micro-indentation, which can consist of a ball shaped indenter on the order of 1 mm in diameter, has been shown to be more effective than nano-indentation for growing a larger whisker and hillock population over a broader area [4,19–21]. This approach increases the overall stress that is transferred to the weaker grain boundaries, and loads would are more cumulative causing the nodule diameter to remain continuous, and, thus, promoting upward growth (i.e., whiskers).

The aim of this study was to develop a simple and cost effective method to rapidly test the whisker growth mitigation efficacy of different coatings. While mitigation of tin whisker growth has been examined previously, limited attention has been given to the development of a rapid method for examining conformal nano-engineered coatings. In the last decade, a variety of such coatings have been commercially applied on a large scale (e.g., coating of solar cells or water proofing electronics with superhydrophobic thin films [22]) due to improved and cost-effective fabrication processes. Such thin coatings do not have potential damage issues caused by thicker films, but have yet to be tested for mitigation of Sn whisker growth. Our accelerated testing approach is to use a broader, micro-scale indentation with continuous loading to induce potential growth of whiskers beyond the directly damaged area. Fig. 1 shows a schematic of the indentation method and conceptual behavior of coating failure and success. As stresses are induced by the IMC and indenter, such as a small ball-bearing, whiskers and hillocks will form. If whiskers or hillocks penetrate the coating then it is considered a failed coating. If whiskers or hillocks grow but do not penetrate the coating (e.g., tenting is observed), then the coating is deemed a success. Herein, we used polydimethylsiloxane (PDMS) to verify the testing method against previous literature results. Once validated, the accelerated testing method was used to determine the potential for a nano-engineered superhydrophobic coating to mitigate tin whisker growth.

2. Materials and methods

2.1. Materials

Cu rod (Alloy 101, Rockwell F84-94, 9.5 mm diameter) was cut into disks 3 mm thick and used as Sn plating substrate. Sn sheet (99.99%, Indium Corp.) was cut into strips at least two times the area of the Cu disk. The Sn plating electrolyte consisted of sulfuric acid (H_2SO_4, 95–98%, Sigma Aldrich 258105), tin sulfate ($SnSO_4$, >95%, Sigma Aldrich 244635), and commercial Sn brightening agents (Electrochemical Products Inc., 180-B and 180-M). Sylguard 182 and silicone elastomer kit (Dow Corning) were used to make PDMS coatings. Polytetrafluoroethylene (PTFE) polymer was synthesized using tetrafluoroethylene (DBD) (DuPont, AF1600, 601S2100-6) and a fluorinated solvent (3M, FC3283).

2.2. Plating

Cu was polished to a final polish using 1 μm Al_2O_3 slurry solution. In between each polishing step, the disks were rinsed with acetone and then sonicated (Branson ultrasonic bath 2800, 40 kHz) in water for 10 min. The Sn anode was polished using 1200 grit and a polishing cloth (Allied Spec-cloth) and then washed with water.

Plating was completed using an 8 mL vertical PTFE reactor (i.e., Fig. 2). The electrolyte was prepared in 100 mL batches. The solution consisted of 87 mL water, 10 mL H_2SO_4, 2.0 mL 180-B, 0.75 mL 180-M, and 2.88 g $SnSO_4$. Fresh solution (8 mL) was used for each plating. Samples were plated using a potential and current of 0.7 V and 0.01 A, respectively, for 15 min. After plating, the

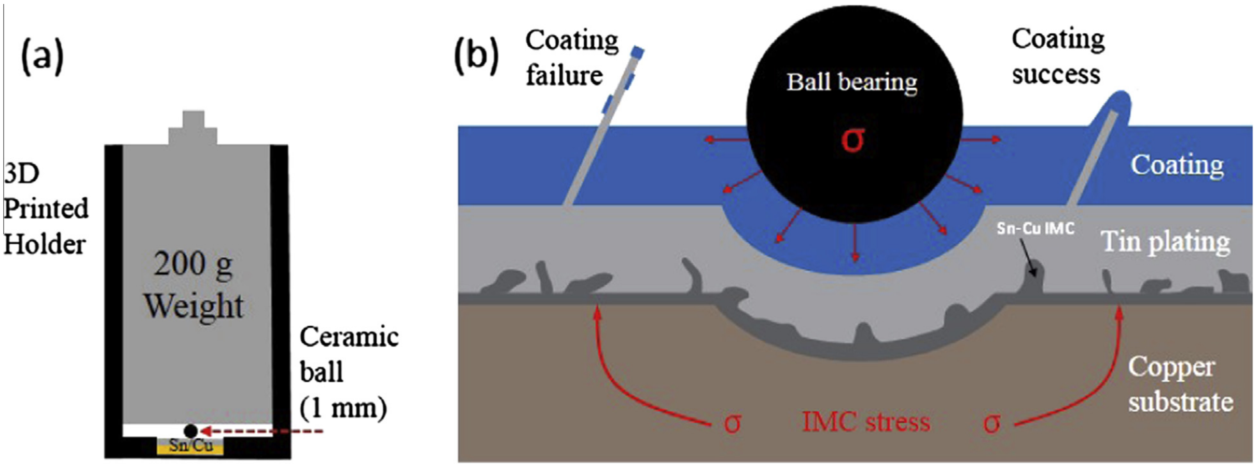

Fig. 1. Schematic of (a) indentation apparatus for accelerated Sn whisker growth and (b) ball bearing indentation and conceptual stress results (σ refers to induced stresses).