Synopsis

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Title of the thesis: Tin Whisker Growth from Electrodeposited Sn films: Developing Materials Science and Mechanics Based Insights.

Pure Sn and Sn-alloy plating are widely used in electrical and microelectronic devices as protective layer to prevent oxidation of Cu conductors and also as Pb-free, Sn based solders. Sn coatings, typically 0.5-10 μm thick, deposited on substrates, e.g., Cu, brass, etc., are prone to spontaneous growth of Sn whiskers under ambient conditions (i.e., without any external stimuli). The growth of whiskers from Sn plating has caused numerous failures in micro-electronic devices, mainly due to short-circuiting (see **Figure 1**), leading to failure of components or devices. Whisker growth is, thus especially very critical in aviation, space and defense applications, where the electronic components are designed for longer life span. Furthermore, due to miniaturization of electronic devices the spacing between adjacent conductors or interconnects can be as small as a few hundred nanometers to a few micrometers, making them more prone to whisker induced short-circuiting (see **Fig. 1**). Minor alloying of Sn with Pb was the principle way for mitigating the whisker growth from Sn plated components; however, due to the recent worldwide acceptance of European Union’s Restriction of Hazardous Substances (RoHS) act, enforcing Pb-free manufacturing, whisker growth has re-emerged as a reliability problem for next generation Pb-free solders and Sn plating finishes.

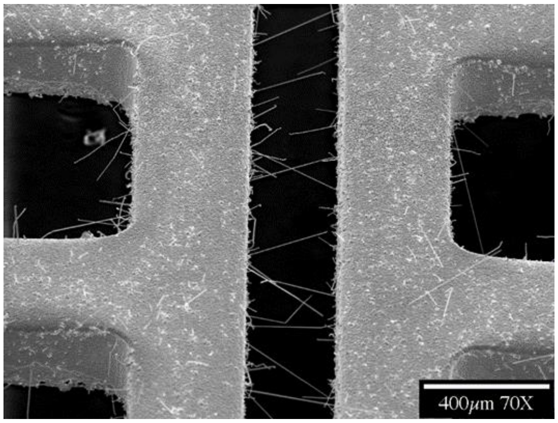
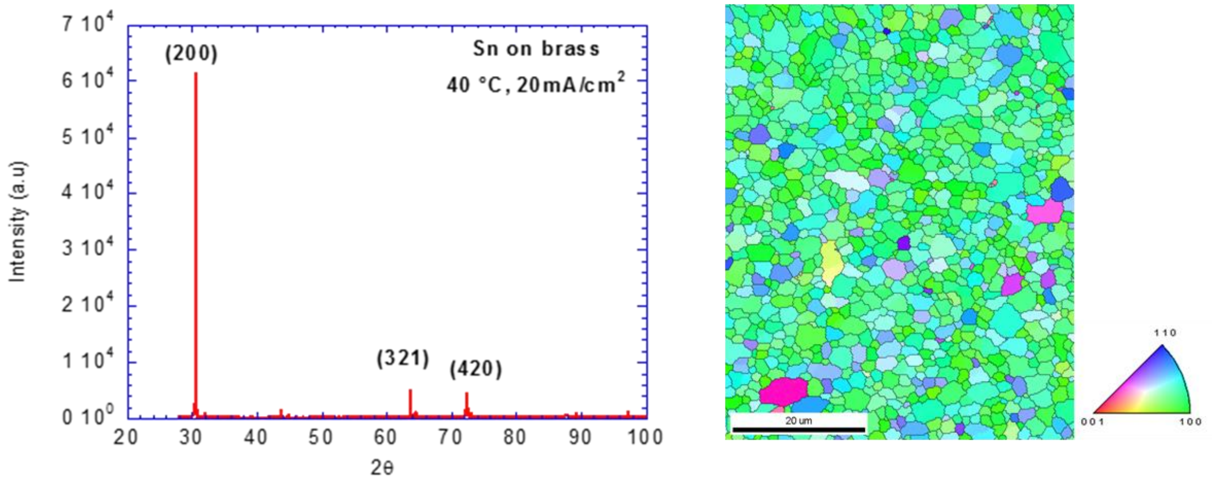


Fig.1: Sn whiskers growing on matte Sn plated Cu lead frame commonly used in small outline integrated circuit (SOIC) lead frame after 3 years. (Image curtsey: NASA space flight center. URL: http://nepp.nasa.gov/whisker)

Despite the decades of research, a universal whisker growth mechanism and hence effective mitigation technique is still not available in public domain. This is mainly due to large number of factors that affect the whisker growth directly or indirectly, making it difficult to devise an experimental procedure, which allows studying effect of one factor at a time while keeping other factors constant. Although many mechanistic models for Sn whiskering have been proposed in the past, the experimental evidences to support them are lacking. For example, recrystallization of whisker grain was proposed by various researchers; however, direct observations confirming whisker grain is indeed a recrystallized grain have never been reported.

Nevertheless, it is well understood that whisker growth is a form of stress relaxation process and diffusion plays important role in the formation of whiskers. Since Sn is extremely anisotropic with tetragonal structure, the stress state of Sn coatings and the diffusion needed for mass transport of atoms vary drastically depending upon the direction of interest. Therefore, it is important to study the role of crystallographic texture (both macroscopic and microscopic) on whisker propensity by systematically varying the crystallographic texture of Sn coating while keeping thickness, grain size, substrate material, and post-deposition storage conditions the same. Better understanding of role of macro- and micro- texture is very crucial before any whiskering mechanism can be proposed. Furthermore, recent studies indicate that role of stresses in Sn coatings driving whisker growth is not fully understood. It is generally accepted that compressive stress in Sn coating is the main factor which drives the whisker growth. However, whiskers were also observed when Sn coating was under tensile stress, making the role of stress a bit controversial. Again, the stresses in Sn have multiple origins and need a systematic approach to understand their origin, quantify them and then relate it to whisker growth. Such systematic approach was never adopted in previous works. Hence, the current thesis aims to address the role of macro- and micro- crystallographic texture, stress regeneration mechanism, nature (i.e., magnitude and sign) of stress and stress gradient in the Sn coatings via systematic variation of texture, post-deposition storage conditions, and substrate composition, including deposition of an interlayer in between Sn coating and the brass or Cu substrate.

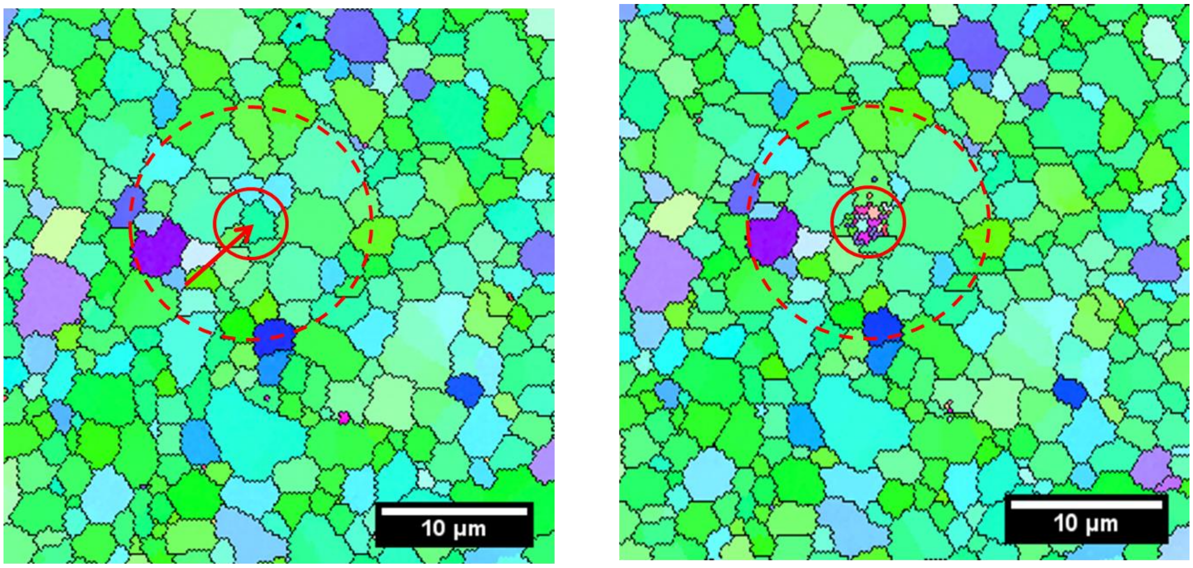
Whisker growth was studied from electro-deposited Sn coatings. The deposition parameters were optimized for producing different thickness and grain orientations. X-Ray diffraction techniques were used to extract macro-texture of the coatings. As shown in **Figure 2**, the macro-texture measurement using XRD and micro-texture measurement using EBSD showed the same dominant and the second dominant orientations. It was observed that current density and deposition temperature (i.e., the two main electro-deposition parameters) significantly influence the crystallographic orientation of the grains. Thus, the global or macro-texture can be manipulated by changing the deposition parameters systematically. It was observed that whisker propensity increases drastically by growth of low index planes, such as (100) and (110), during deposition. Hence, proper selection of deposition parameters that lead to growth of high index planes can be used to suppress the whisker growth.



(a) (b)

Fig. 2: (a) X-ray diffraction peak profile, and (b) EBSD grain orientation map of a Sn coating deposited on brass at a constant bath temperature of 40 °C and a current density of 20 mA/cm^2. Both macro-texture and micro-texture indicate same dominant orientation of grain, i.e. (100).

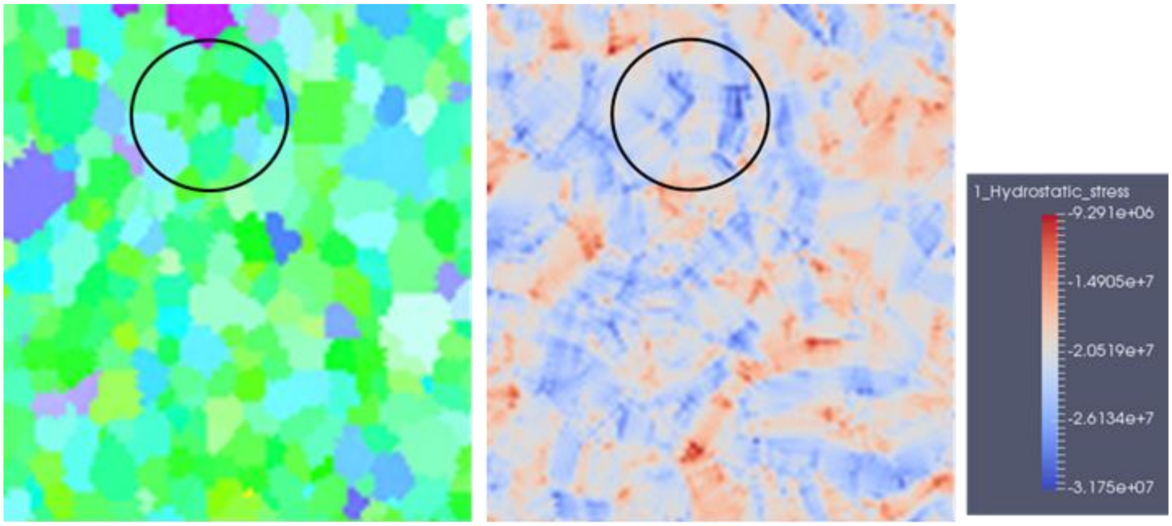
Furthermore, micro-texture surrounding whisker grain was studied using EBSD technique by observing the same set of grains surrounding a whisker before and after whiskering. OIM maps of several whisker regions clearly indicate that whiskers preferentially grow from low index planes, such as (100), etc., as shown in **Figure 3**. Furthermore, using orientation dependent stiffness mapping, it was noticed that whiskers preferentially grew from regions of soft oriented grains (low modulus) surrounded by hard orientations. In addition, grain boundary misorientation analysis revealed presence of high fraction of high angle grain boundaries in the vicinity of whisker grain. In addition, it was observed that whisker grew from pre-existing grain and not from the recrystallized grain. Also, grain boundary sliding was not observed as a pre-requisite for whisker growth in Sn coatings on brass substrate.



(a) (b)

Fig. 3: Orientation image map of Sn coating: (a) before whisker growth (i.e., within 24 h after deposition) and (b) after whisker growth (after 10 days of aging under ambient conditions). The arrow indicates the whisker grain. First and second nearest grains are shown using solid and broken circle, respectively.

The local stress field around the whisker grain will also play a crucial role in whisker growth. Therefore, local stress field around whisker site was simulated using crystal plasticity simulation by incorporating grid resolved spatial description of orientation in terms of Euler's angles. The crystal plasticity model included slip systems of Sn and other material parameters, such as anisotropic elastic stiffness constants, critical resolved shear stresses for different slip systems, etc. Thus, the slip in individual grain was accounted following homogenization to maintain compatibility at grain boundaries. It has been observed that, as shown in **Figure 4**, high compressive hydrostatic stresses develop near the whisker grain, most likely at high angled grain boundaries and triple points.



(a) (b)

Fig. 4: (a) The geometry used in the crystal plasticity simulation and (b) the hydrostatic stress distribution around a whisker grain. Whisker grain location is indicated by circle in (a) and (b). The legend in (b) shows the magnitude of hydrostatic stress. The geometry for a crystal plasticity simulation was imported from EBSD generated orientation image map.

The stress in Sn coatings may originate from many factors, such as residual stress inherent to electro-deposition, diffusion of substrate atoms (Cu, Zn, etc.) into the coating, formation of interfacial intermetallic compound (IMC) layer, segregation of impurities at Sn grain boundaries, formation of surface oxide layer, and coefficient of thermal expansion (CTE) mismatch between in Sn and substrate as well as between differently orientated grains of Sn. Therefore, it is important to understand the dominant stress regeneration mechanism responsible for whisker growth. To identify dominant mechanism, which can continuously regenerate the compressive stress in Sn, samples deposited under fixed electro-deposition conditions were exposed to different post-deposition storage conditions, such as isothermal aging at room temperature, 50 °C, 150 °C, and thermal cycling from -25 to 85 °C with and without hold time at the highest temperature. It has been observed that Cu_6Sn_5 IMC growth due to the inter-diffusion of Cu and Sn atoms is the dominant mechanism responsible for whisker growth. Both growth kinetics and morphology of IMC have a significant impact on whisker growth. As shown in **Figure 5**, the role of CTE mismatch in regenerating compressive stresses in Sn coatings on brass substrate for whisker growth is highly limited.

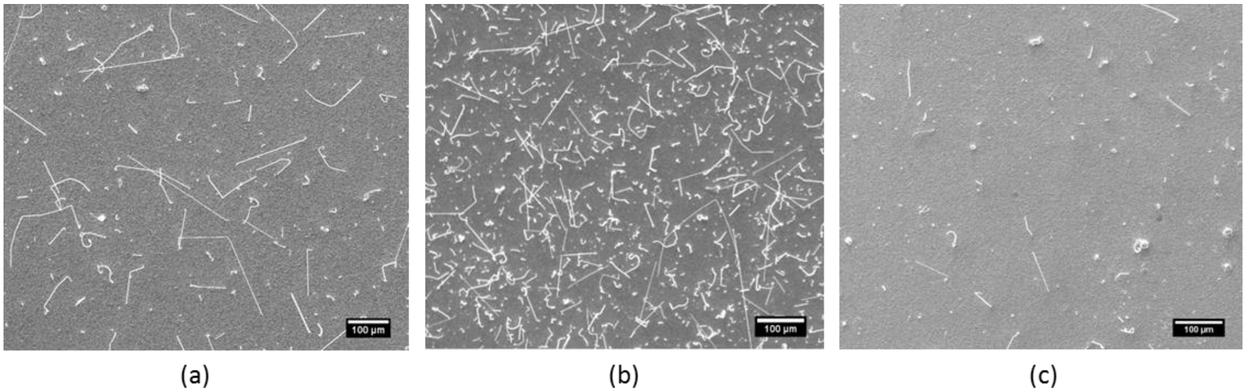
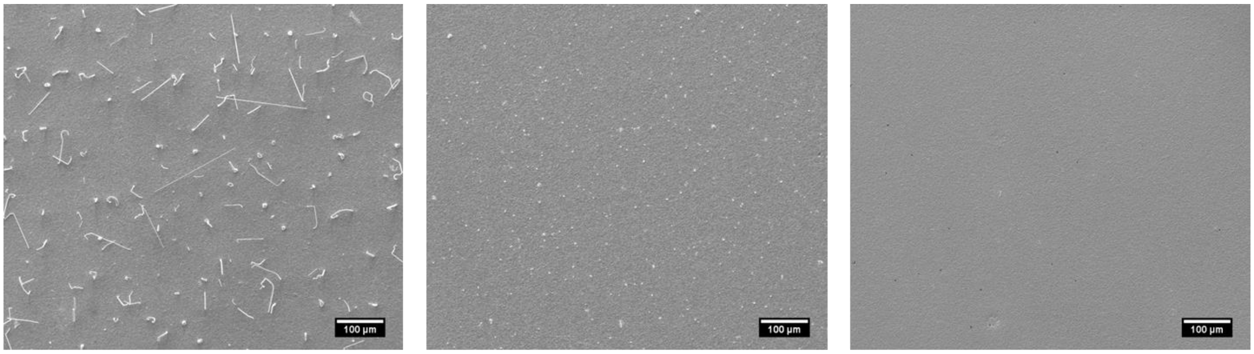


Fig. 5: Whisker growth from Sn coatings deposited on brass substrate with fixed deposition parameters: (a) isothermal aging at room temperature for 30 days, (b) isothermal aging at 50 °C for 30 days and (c) thermal cycling from -25 to 85 °C for 100 cycles, without any hold at high temperature.

The substrate composition as well as the underlayer of metallization will also affect the inter-diffusion between Sn and the substrate atoms and therefore IMC growth, which is mainly responsible for whisker growth in Sn coatings on brass or Cu substrates. The effect of substrate composition on whisker growth was studied by using pure Cu, brass (65 wt. % Cu 35 wt. % Zn) and Ni (bulk and electro-deposited underlayer) as substrate. As shown in **Figure 6,** whisker growth is more rapid if brass substrate is used instead of pure Cu. Whiskers are not formed when Sn is deposited on either bulk Ni or when Ni underlayer was electro-deposited on brass or Cu substrates prior to Sn deposition. Ni underlayer effectively stops the Cu diffusion into Sn, thus avoiding the growth of Cu_6Sn_5 (which puts Sn coatings under compressive stress). Thus, it is clear that continuous formation of Cu_6Sn_5 at the interface provides long term driving force for whisker growth.



(a) (b) (c)

Fig. 6: SEM micrographs of Sn coatings after 3 days of aging at 50 °C: (a) Sn on brass, (b) Sn on Cu and (c) Sn on brass with Ni underlayer.

Since the whisker growth is a stress driven phenomenon, it is important to understand the stress evolution in Sn coatings. Stress state of the Sn coatings was studied using custom-built laser curvature set-up with multi-beam optical stress sensor (MOSS). This allowed monitoring of curvature change of the coating-substrate system in real time and the bulk average stress was calculated using Stoney's equation. In addition, glancing angle X-ray diffraction was employed to analyze stress in the top surface region of the coating. The variation of glancing angle allowed probing strain at different penetration depths. A shown in **Figure 7,** both the bulk stress and the stress in only near surface region evolve with time. The residual bulk stresses in Sn coatings are tensile immediately after deposition. The residual stresses relax very quickly upon room temperature aging and become compressive. The bulk of Sn coatings on brass substrate progressively become more compressive upon continued aging. However, stresses in Sn coatings deposited on brass substrate with Ni underlayer saturate quickly at only -10 MPa. Surprisingly, stress in the top-most region of Sn coating measured using XRD evolve differently. The surface of Sn coating deposited on brass substrate is compressive initially and progressively become more tensile, while the initial compressive stress in the sample with Ni underlayer increase a bit and saturate at around -20 MPa. Therefore, the surface of the Sn coatings with Ni underlayer is always more compressive than the bulk stress in the Sn coating. Therefore, a negative stress gradient for the diffusion of Sn atoms towards surface is never established and whiskers do not grow in these Sn coatings. Interestingly, through thickness voids are observed in the Sn coatings on Ni. Contrarily, in Sn coatings without Ni underlayer after 170 h of aging, the surface stress becomes more tensile than the bulk of the Sn coating, favoring continuous migration of atoms from the highly compressed region near interfacial Cu_6Sn_5 IMC layer to the stress free whisker root. Aforementioned observation indicates the crucial role of negative stress gradient for mass transport of atoms required for whiskering.

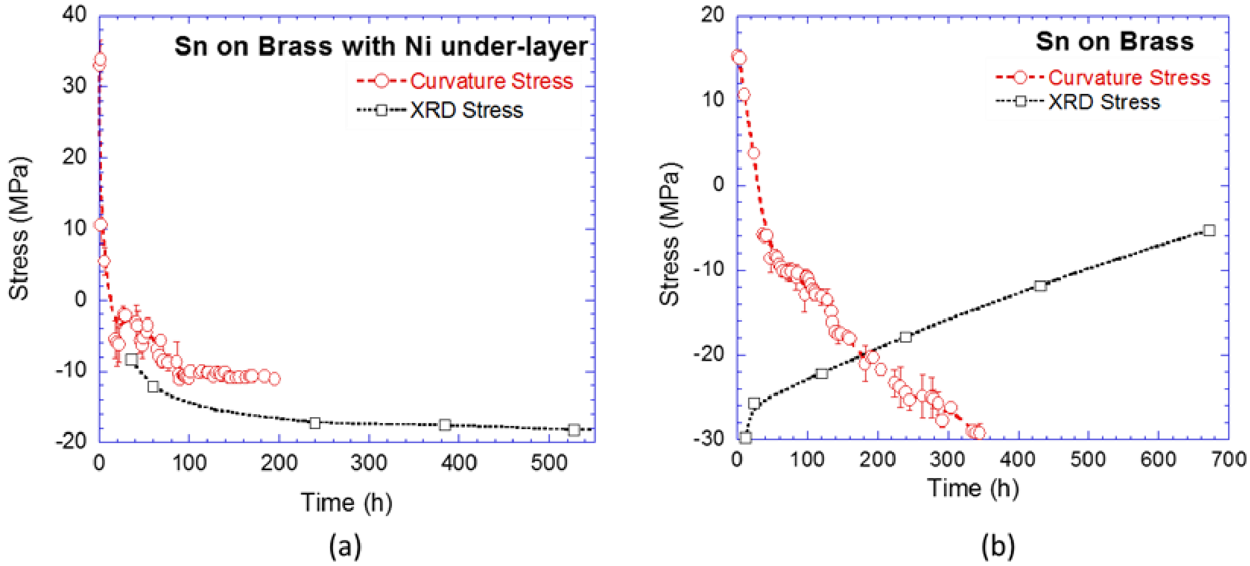


Fig. 7: : Evolution of bulk stress and stress in top 0.7 μm region near surface: Sn coating on brass substrate (a) with Ni under-layer (i.e., no whiskers, but with voids), and (b) without any interlayer (i.e., with whiskers).

The importance of stress and stress gradient was further studied by analyzing the effect of externally imposing stress and stress gradient on whisker growth. The stresses were applied using a three-point bend setup, as shown in **Figure 8**. It has been observed that, externally applied stress accelerates the whisker growth. This is mainly because applied stress alters the diffusion kinetics and growth of Cu_6Sn_5 intermetallic compound at the interface. However, the coating under tensile stress shows more whisker growth as compared to the coating under high compressive stress. This is attributed to the fact the coating under tensile stress is under higher negative stress gradient. Therefore, it is proposed that out-of-plane stress gradient is more important rather than the sign and the magnitude of stress.

(a) (b)

Fig. 8: (a) The schematic illustration of method used to apply compressive and tensile stress and stress gradient on Sn coatings using three-point bending, and (b) the photograph of the actual three-point bending setup along with sample.