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Methods for fast, reliable growth of Sn whiskers☆

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ABSTRACT

We report several methods to reliably grow dense fields of high-aspect ratio tin whiskers for research purposes in a period of days to weeks. The techniques offer marked improvements over previous means to grow whiskers, which have struggled against the highly variable incubation period of tin whiskers and slow growth rate. Control of the film stress is the key to fast-growing whiskers, owing to the fact that whisker incubation and growth are fundamentally a stress-relief phenomenon. The ability to grow high-density fields of whiskers (10^3–10^6/cm^2) in a reasonable period of time (days, weeks) has accelerated progress in whisker growth and aided in development of whisker mitigation strategies.

1. Introduction

Tin whiskers are single crystal electrically conductive eruptions that spontaneously grow from the surface of Sn plated films. High-aspect ratio Sn whiskers are typically cylindrical in shape, 1–5 μm in diameter and between 1 and 500 μm in length, but have been reported to grow as long as a few millimeters (Fig. 1). Whiskers are usually generated on thin metal films (0.5 to tens of microns) which have been deposited on a substrate material, though whiskers have also been observed infrequently to grow from bulk materials. They can be straight, kinked, or even curved. Metallic film deposits can also have other types of eruptions that are quite different in appearance from the high-aspect ratio whisker eruptions. These are commonly referred to as flowers, extrusions, hillocks and volcanoes. Generally, they are of lower academic interest when compared to the longer, high-aspect ratio whiskers. Most of the work presented here will focus on Sn whiskers, since they are the dominant whisker problem for electronic components today. Sn, however, is not the only existing whisker-forming material, for cadmium, zinc, indium, aluminum, gold, and lead have also been observed to produce whiskers.

Whiskers are problematic for electronic assemblies since they can breach components and create short circuits. The general risks of Sn whiskers are stable short circuits in low voltage, high impedance circuits. In such circuits there may be insufficient current available to fuse the whisker open and a stable short circuit results. At atmospheric pressure, if the available current exceeds the fusing current of the whisker, the circuit may only experience a transient glitch as the whisker fuses open. In plasma and vacuum environments, if currents above a few amps are available and the supply voltage is ~12 V, the whisker will fuse open but the vaporized tin may initiate a plasma that can conduct over 200 A. An adequate supply of tin from the surrounding plated surface can help sustain the arc until the available tin is consumed or the supply current is interrupted such as occurs when a protective fuse element interrupts. This phenomenon is reported [1,2] to have occurred on at least three commercial satellites, resulting in blown fuses that rendered the spacecraft non-operational. Whiskers can also break loose and bridge isolated conductors or interfere with optical surfaces.

Metallic whisker formation first became a subject of interest as early as the 1940s, immediately after World War II. Electroplated cadmium was the first to grow whiskers long enough to short out adjacent capacitor plates in electronic components, first reported by Cobb [3] in 1946. In 1948, Bell Telephone Corporation experienced failures on channel filters used to maintain frequency bands in multi-channel telephone transmission lines. Failure analysis showed that Cd whisker formation was the root cause of the channel-filter failures. Bell Laboratories then initiated a series of long-term investigations into the general topic of whisker formation, which was first reported in 1951 by Compton et al. [4]. The research established that whisker formation occurred spontaneously, but not only on Cd electroplating. Whisker growth was also found on electroplated Zn and Sn. The Compton paper provided the first summary statements that would be used as a guide to future whisker research. The conclusion was that whisker growth is not limited to electrodeposited coatings and may also be found on solid metals. Much of the research since that time has focused on electroplated Sn and Sn-alloys on various substrates, since Sn and Sn-alloy electroplating became the plating of choice for electronic components due to the

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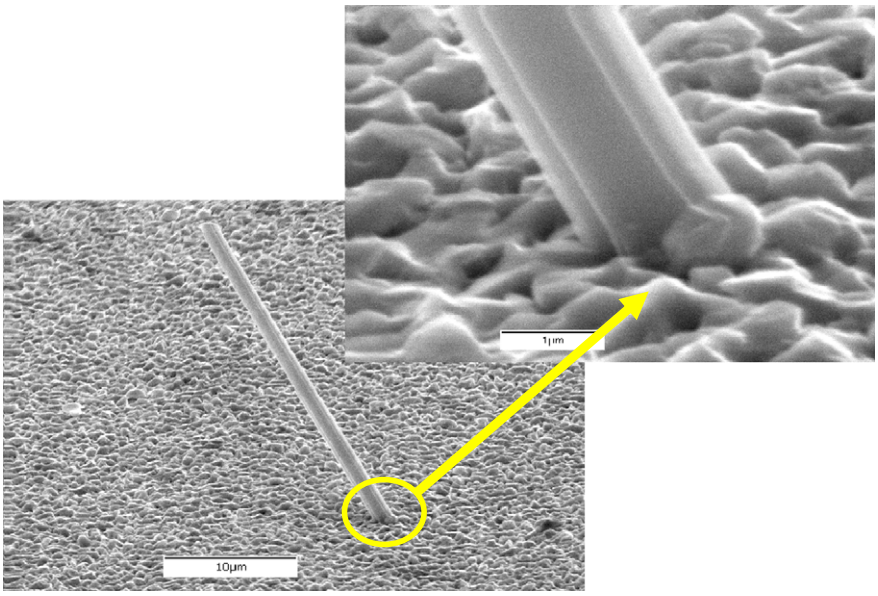


Fig. 1. Typical appearance (SEM) of a high-aspect Sn whisker.

favorable combination of contact resistance, corrosion resistance, low cost, and solderability.

Current interest in whiskers originates from the worldwide initiative to eliminate the use of lead (Pb) in electronics, which had been known for decades to greatly suppress Sn whisker formation. International legislation has driven the industry to consider high tin alternatives to the widely used Sn–37Pb alloys used for plating and solder [5,6]. Pure tin plating is seen by the industry as a potentially simple and cost effective alternative to the standard Sn–Pb plating and many manufacturers have been offering pure tin plated components as a standard commercial (and in some cases high reliability) product for years. Continuing reports of tin whisker induced failures (see Table 1) coupled with the lack of an industry-accepted understanding of tin whisker growth and test methods to identify whisker-prone products has made blanket acceptance of pure tin plating a risky proposition for high reliability systems.

The original rationale behind eliminating Pb from electronics assemblies was the exponential sales growth in consumer electronics such as computers and cell phones. Along with the explosive growth of electrical units in the field was the problem of how to dispose of them at their end-of-lifetime. The fear was that Pb from thousands of buried circuit boards in landfills posed a hazard to nearby water sources. Pb-free regulations currently affect nearly all electronic products (an exception is granted for certain high-reliability military use devices). Sn whiskers have therefore re-emerged as a major reliability concern in electronic systems. The problem has further been exacerbated by the continued industry demands for smaller and faster devices, with higher packing densities and smaller critical dimensions. Under these conditions, whiskers pose even more of a threat.

2. Challenging aspects of whisker studies

One of the complications when studying whiskers is the issue of time. Whiskers have been observed to grow within days in some cases, but may take up to years and even decades before growing long enough to cause failures in electronic systems. This means that an electronic component that is whisker-free one day can be whisker-prone the next day, creating a reliability nightmare scenario. It is this dormancy, commonly known as the incubation period, that distinguish whiskers from other surface plating defects such as nodules or dendrites, which may be roughly similar in appearance to whiskers but present on the surface immediately after plating. This attribute of whisker growth is particularly frustrating since, in order to complete any kind of meaningful experiment, very long time periods may be necessary to grow whiskers.

It is important not to take the incubation period lightly. Sn plated electronic systems that may seem fine and functional for many years remain under the threat of whisker growth. In 1976, Dunn (of the European Space Agency) [7,8] released a set of publications strongly recommending that surfaces susceptible to whisker growth (such as Sn) be excluded from spacecraft design. Not all satellite manufacturers followed his suggestion and, over a decade later, in 1990, several

Table 1
Documented Sn whisker failures (1986–2003) (courtesy of NASA Electronic Parts & Packaging (NEPP) program).

Year	Application	Industry	Whiskers on?
1986	Heart pacemakers	Medical (RECALL)	Crystal can
1986	MIL aircraft radar	Military	Hybrid package lid
1987	MIL/aerospace PWB	MIL/aerospace	PWB traces
1988	Missile program "A"	Military	Relays
1989	Missile program "B″	Military	Electronics enclosure
1992	Missile program "C″	Military	Xsistor package + standoff
1993	Govt. electronics	Govt. systems	Transistor, diode, lug
1996	MIL aerospace	MIL aerospace	Relays
1998	Aerospace electronics	Space	Hybrid package lid
1998	Commercial satellite #1	Space (complete loss)	Relays
1998	Commercial satellite #2	Space	Relays
1998	Commercial satellite #3	Space	Relays
1998	Military aerospace	Military aerospace	Plastic film capacitor
2000	Missile program "D"	Military	Terminals
2000	Commercial satellite #4	Space (complete loss)	Relays
2000	Commercial satellite #5	Space (complete loss)	Relays
2000	Power mgmt modules	Industrial	Connectors
2001	Commercial satellite #6	Space	Relays
2001	Nuclear power plant	Power	Relays
2001	Hi-Rel	Hi-Rel	Ceramic chip caps
2002	Commercial satellite #7	Space	Relays
2002	Military aircraft	Military	Relays
2002	Electric power plant	Power	Microcircuit leads
2002	GPS receiver	Aeronautical	RF Enclosure
2002	MIL aerospace	MIL aerospace	Mounting hardware
2003	Commercial electronics	Telecom	RF Enclosure
2003	Telecom equipment	Telecom	Circuit breaker
2003	Missile program "E"	Military	Connectors
2003	Missile program "F"	Military	Relays

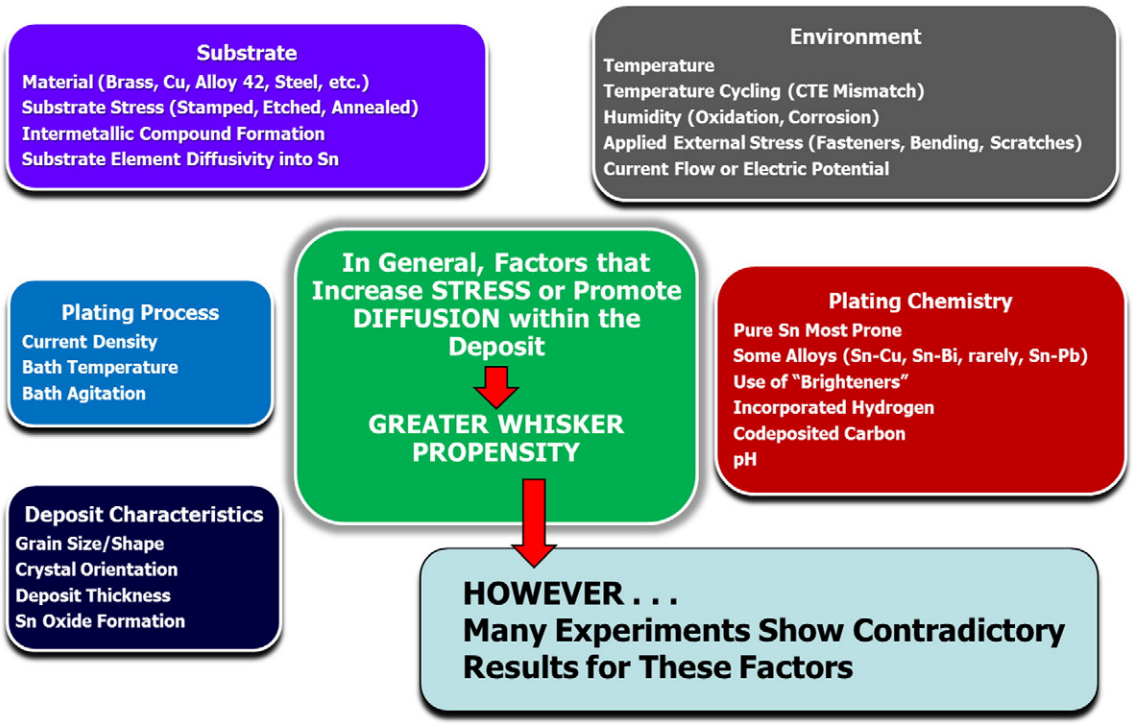


Fig. 2. A multitude of factors influence whisker growth (courtesy of NASA Electronic Parts & Packaging (NEPP) Program).

commercial spacecraft failed due to Sn whisker problems. The U.S. military first become aware of the incubation of Sn whiskers and their potential problems when the USAF was inspecting failed circuits in 12 year old radar systems and found whiskers up to 2.5 mm in length growing on Sn-plated lids of hybrid circuits [9]. Another incident where whiskers arose after a long period of dormancy was found in March 2000 in 10 year old General Electric relays [10].

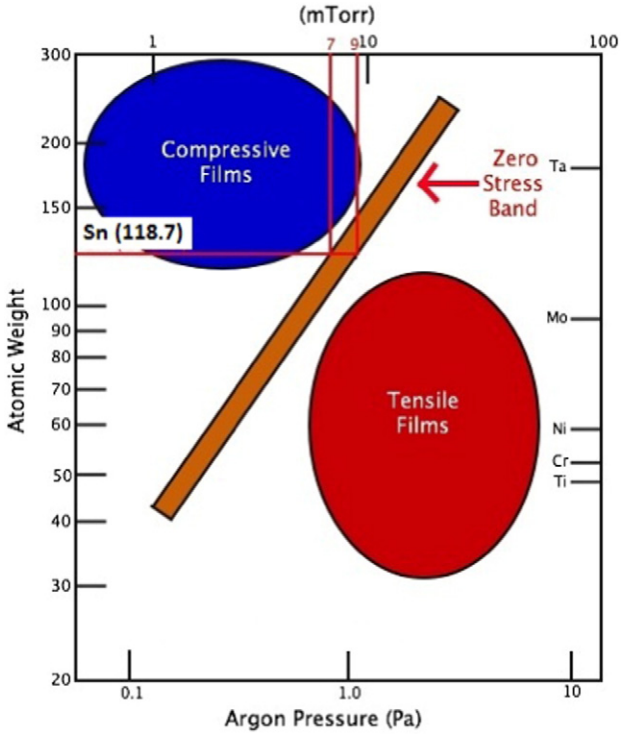


Fig. 3. Magnetron sputter system conditions which produce intrinsic net compressive and tensile films. For the case of Sn films, Ar pressures <7 mTorr produce compressive films and tensile films are produced >9 mTorr. Adapted from [19].

A second frustrating factor in whisker studies is the highly variable growth rate of whiskers. Whisker growth rates [11] range from 0.03 to 9 mm/yr which means their growth is highly variable and unpredictable. For example, in 1954, Fisher et al. [12] reported a Sn whisker growth rate of 10,000 Å/s under a clamping pressure of 7500 lbf/in^2 on Sn plated steel. The growth rate was essentially linear which at some point in time went to zero. He also reported growth rates for spontaneous Sn whisker growth (no clamping pressure) at ~0.1 to 1.0 Å/s [13]. However, in 1964, Pitt and Henning [14], also using clamp pressure on hot-dipped tin deposited on Cu and steel, reported the highest whisker growth rate at 593 Å/s with 8000 lbf/in^2 of pressure, with whisker growth rates that decreased with time. The wide range of variation in whisker growth rates makes whisker studies difficult, as one doesn't know how long to wait to see whiskers, how fast whiskers grow, and when whiskers will stop growing. Other contributing complications include the fact that not all of the variables affecting whisker growth are known and the recognized variables are not always reported accurately when data is published. Further, current test methods cannot correlate whisker growth in test conditions to actual field conditions; therefore, test results cannot be used to predict whisker growth in other environments or for longer durations. There is a need to compare whisker growth data derived in controlled, short-term environmental tests to long-term field exposures in order to quantify whisker-reliability predictions for electronic devices.

One of the goals in this work was to minimize the time to whiskers by developing quick and reproducible methods for growing high density fields of whiskers for a variety of research purposes in a timely (weeks) fashion. Electroplating is the current thin film method of choice in industrial processes; however, whisker growth can take up to years and even decades in many electroplated Sn films. Studies utilizing already-grown industrial and/or anecdotal whiskers offer only limited perspectives for whisker research. Last, there is a pragmatic reason for the requirement of fast, reproducible whisker growth which affects academic researchers. Imagine explaining to a young graduate student

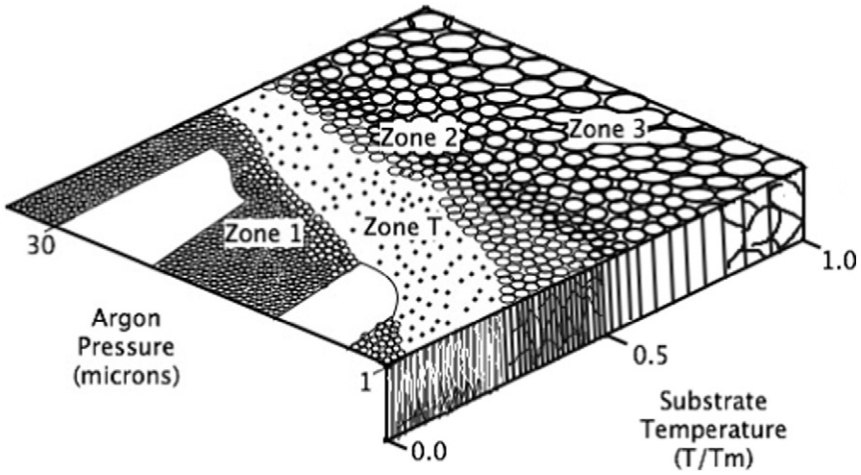
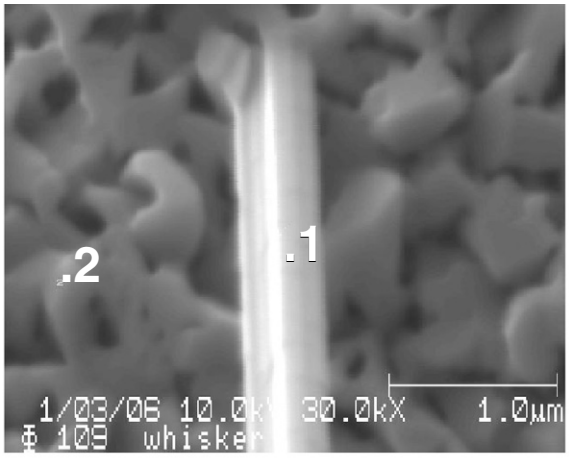


Fig. 4. The structure zone scheme. As the substrate (film) temperature during deposition increases, the size of the grains increases. For the case of Sn, deposition at room temperature corresponds to a homologous temperature of $T/T_m = 0.6$, producing columnar film growth near the boundary between Zone 2 and Zone 3. From [21].

whom you are recruiting for studies on whiskers "well, you might have to wait around a couple years before we have a whisker to study, but even that is not guaranteed."

3. Factors affecting tin whisker growth

There is currently no general consensus on the underlying mechanism(s) of whisker incubation and growth. The science of whiskering is still being worked out. A great deal of controversy and contradictory information regarding the key factors that affect whisker formation still exists. Several attempts have been undertaken/currently running to develop accelerated test methods to determine the propensity of a particular system and its environment to form whiskers. To date, however, there are no universally established test methods for evaluating whisker susceptibility. In fact, much of the experimental data compiled throughout the years has produced contradictory findings regarding which factors accelerate or retard whisker growth.



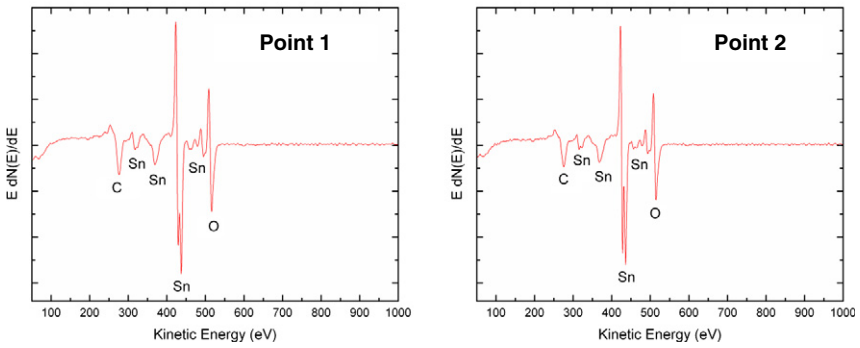


Fig. 5. Auger analysis of two positions both on (Pt 1) and off (Pt 2) a Sn whisker, showing no evidence of the brass substrate. A depth profile into the bulk of the whisker also showed no evidence of Cu or Zn. The native surface oxide whisker exoskeleton thickness was measured to be ~20 Å.

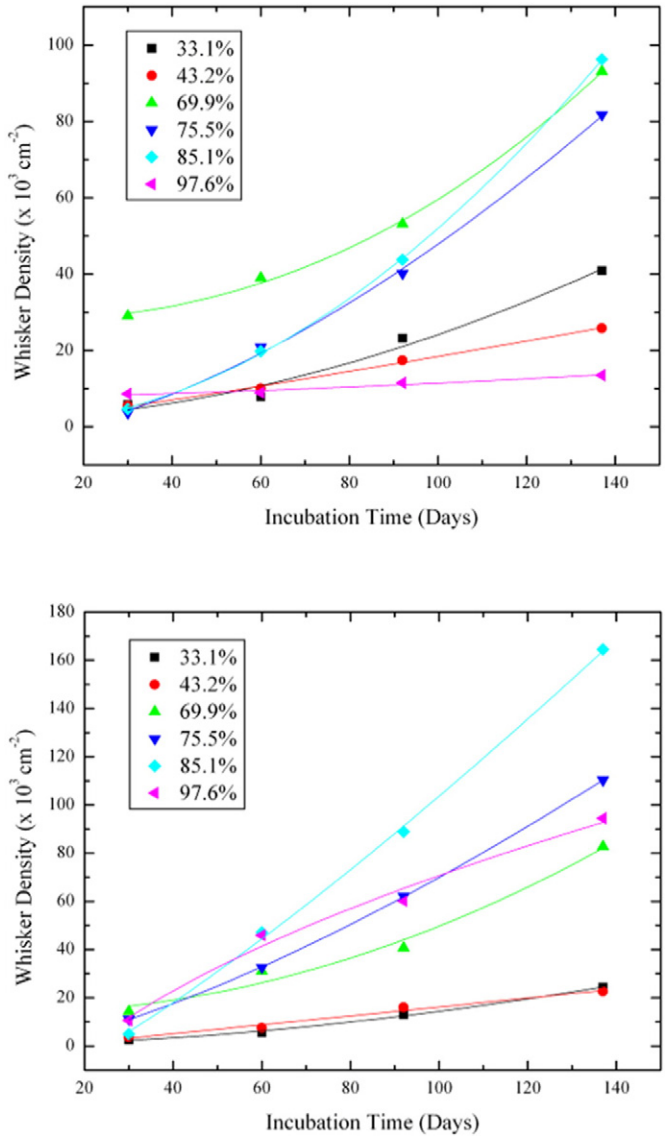


Fig. 6. Whisker density vs. incubation time for 1500 Å Sn film deposited on brass (top) and Si (bottom) exposed to various relative humidity environments. Data from [41].

That being said, there are a number of commonly agreed upon variables that influence whisker formation (Fig. 2). Most researchers agree that compressive stress in the Sn film is the fundamental driving force behind whisker growth [15]. This stress may be intrinsic stress, which is stress distributed in the as-plated Sn film with its associated texture (grain size and crystallographic orientation) [16,17] or, extrinsic stress, arising from chemical reactions between the Sn-film and the substrate (intermetallic compound formation), uneven diffusion between the substrate material and tin film, mechanical processes such as bending, forming, and thermo-mechanical stresses (CTE mismatch), plating chemistry (bright tin) and/or impurities introduced during film deposition, oxygen diffusion and/or oxide formation on the surface, and even storage or operating environment conditions (such as corrosion possibilities).

This is how we measure and count whiskers. Although tedious and labor intensive, most whisker researchers continue to rely on manual whisker counting in an SEM. There is still no automated method to detect, count, and measure whiskers and optical microscopes have limited depth of focus, which is a weakness for whisker studies. Thus, throughout the experiments herein, we have used a SEM to count whiskers, accounting for all whisker lengths ranging from 2 μm and greater. Unless otherwise stated, the whisker densities are determined by manually counting whiskers in the SEM over ten equal areas (~275 μm × 275 μm) representative of the surface in question as a whole. Each whisker counted is also measured for length from a single, top-down view (uncorrected for angle foreshortening [18]). As with any counting scheme, the "random error" becomes the statistical error associated with sampling or counting which goes as ~ $\sqrt{N}$ where N is the number of counts. Due to the manual procedure of counting a small representative sample of the total number of whiskers, standard deviation values for quantities such as whisker density, length, and mode (the most frequently observed whisker length) are inherently large.

4. Whisker growth by magnetron sputtering techniques

Modern electronics assembly processes employ thin films grown by electrochemical deposition, which introduces several difficult-to-control variables such as brighteners, bath conditions, purity of the feedstock, and incorporation of impurity atoms during film deposition. It is advantageous to avoid these factors when growing research-grade films. We found that one key to producing fast whisker growing Sn films was to look backwards. In 1989, Thornton and Hoffman [19] studied sputter deposition under argon plasma for many different metal films and identified a simple system of "dialing in" various amounts of intrinsic thin film stress by changing the background gas pressure in the sputtering system. They did this by determining the critical pressures for the compressive-to-tensile stress transition in thin films as a function of atomic mass. This plot, re-drawn in Fig. 3, was used to determine the sputtering pressures necessary to produce thin Sn films under states of compression, tension, and zero stress. For the case of Sn films, compressive stress results by using a background Ar pressure ranging from ~1–6 mT and tensile stress results when using 10–100 mT. Even a "no stress" film state can be produced by the Thornton approach, but it has a fairly narrow, 7–9 mT, gas pressure range which is difficult to achieve and control without practice. Our sputtering system is a 30-year old Varian magnetron sputtering system similar to Thornton's which has been retrofitted with modern sputtering guns, turbo-molecular pumps, and mass flow controllers.

The creation of sputtered film stress states is based on the packing density of Sn during sputter deposition. Sputtering at high Ar pressure leaves the depositing Sn atom with low kinetic energy, which produces a low packing density in the film. This leaves the deposited atoms far apart, creating a net force of attraction between them, which shrinks the film and produces a concave curvature in the substrate (tensile stress). Contrastingly, sputtering at low Ar pressure gives the depositing Sn atoms high kinetic energy, which leaves the deposited atoms packed tightly and causes them to exert a force of repulsion against each other (due to overlapping electron orbitals). This expands the film and results in a convex curvature in the substrate (compressive stress). A complementary perspective is that Sn wants to expand with respect to the substrate and is thus in a state of compressive stress due to the constraint of the substrate.

Typical whisker densities created when sputtering ~0.2 μm Sn films on a silicon wafer show that, after three months of incubation at room temperature, high whisker densities are observed under both tensile (12,000 whiskers/cm^2) and compressive (16,000 whiskers/cm^2) stress conditions, with a minimum whisker density generated in the zero stress (4000 whiskers/cm^2) condition [20]. It is likely that the zero stress condition produced whiskers due to the difficulty in achieving the narrow range (7–9 mTorr) of background pressures necessary to produce the zero stress state. Relative average whisker lengths were 56 μm (tensile stress); 4 μm (compressive stress); and 1.5 μm (zero stress). The Sn films sputter deposited in this way produce bright, rather than matte, Sn structures with small (<1 μm) grain sizes. It is known that, while all three types of Sn thin films (matte, satin bright, and bright) will grow

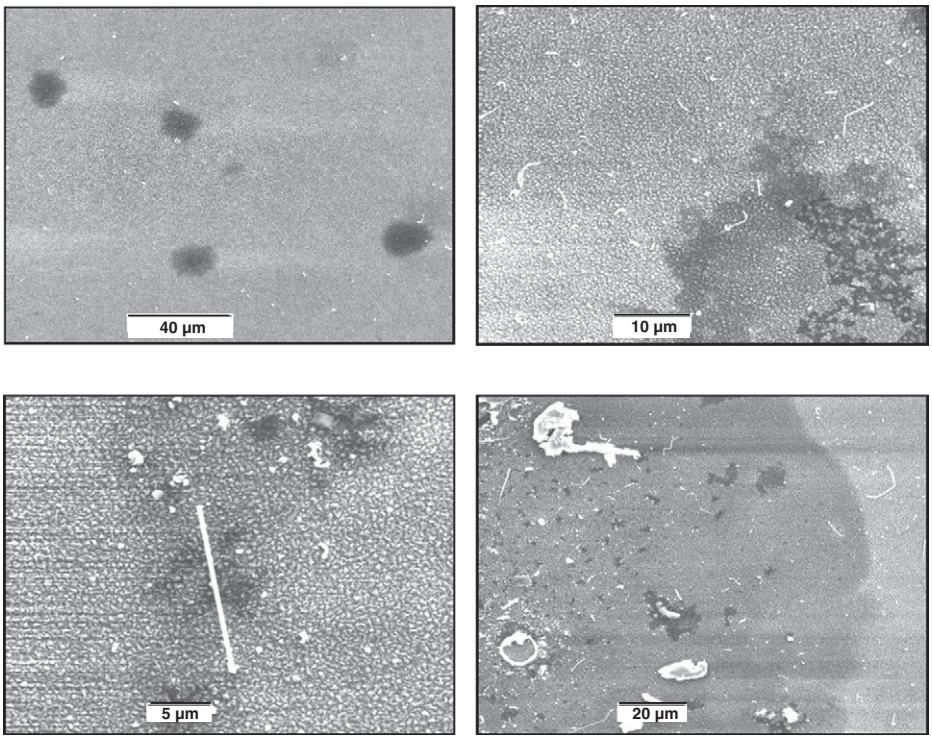


Fig. 7. Whiskers observed at 85% RH (left) on brass and (right) on Si.

whiskers, highly stressed bright tin films are much more prone to whisker formation than are satin bright and matte tins. These characteristic results have proven to be reproducible for our sputtering system and it is rare that we are not able to produce similar whisker densities.

Speaking of grain size, an additional advantage in using magnetron sputtering to produce Sn whiskers is that the width and shape of Sn whiskers depends on the microstructure of the Sn film. For the case of sputtered films, it is possible to modify the deposited grain size by sputtering at temperatures higher than room temperature. The resultant structure zone scheme (Fig. 4), described in a series of papers by Thornton and Hoffman [21] in the 1970s, shows that not only the grain size, but other morphological aspects of the deposited film (such as the degree of columnar growth) can be varied by a combination of temperature and background argon pressure in the sputter system. In Fig. 4, as the ratio of the film temperature T_s to the melting point temperature T_m increases, the size of the individual grains increase. Thus, by increasing the temperature of the substrate while depositing the film, it is possible to control the size and shape of the grains. By extension, one should be able to see a difference in whisker growth with different zone samples. Most of the work presented by our group has been done at room temperature, thus $T_s/T_m = 0.6$. This places the majority of our work in Zone 2. Due to the low melting point of Sn (232 °C), there is not much temperature space to explore; nevertheless, we have worked [22] at two elevated substrate temperatures given by $T_s/T_m = 0.75$ (106 °C) and $T_s/T_m = 0.85$ (156 °C). These two (Zone 3) temperatures allow for observation of grain size effects on the growth of tin whiskers in comparison to Zone 2 and have allowed us to grow tailored whiskers for experiments involving conformal coatings.

Table 2
Coefficient of Thermal Expansion (CTE) Differences Sn vs. Various Substrates.

Substrate	CTE (10^{-6} K^{-1})	ΔCTE_{Sn}	$\%\Delta CTE_{Sn}$
Sn	23.4	0	0
Al	22.2	1.2	5.1
Ag	19.5	3.9	16.6
Brass	18.7	4.7	20.1
Zn	29.7	6.3	26.9
Ni	13.0	10.4	44.4
Ta	6.5	16.9	72.2
GaAs	5.7	17.7	75.6
Si	5.1	18.3	78.2
InP	4.6	18.8	80.3

5. Verification of pure Sn whiskers by Auger spectroscopy

In our early work on Sn whiskers grown from sputtered Sn films, it was important to verify that the whiskers produced were pure Sn and not "pulling up" the substrate during growth and forming a Sn alloy whisker. This was especially interesting after we observed that Sn whiskers > 500 μm in length were growing from sub-micron film thicknesses of Sn. Sn whiskers had long been presumed to be pure Sn, largely as a conclusion of comparative X-ray diffraction studies on substrates both with and without whiskers. The limitation of conventional diffraction approaches, however, is that the spot size of an X-ray system is substantially larger than a typical Sn whisker and conclusions on material properties are based on area-averages over a large portion of the substrate surface. A direct, compositional measurement of the surface and bulk of a Sn whisker was needed, made possible by using high lateral resolution Auger electron spectroscopic (AES) measurements on high aspect ratio Sn whiskers, grown from Sn on a brass substrate.

There was an early (1980) attempt [23] at doing AES on Sn whiskers using a lower-resolution Auger spectrometer on nodules and whisker-like features grown on various combinations of Sn (1–5 μm) on electroplated brass. The AES spectra in this work showed the existence of Zn on both the Sn substrate and whisker surfaces which were attributed to Zn surface impurities. But the existence of surface impurity Zn confuses the issue of whether the whiskers contained brass from the brass substrate. Further, the analysis was performed at an abnormally high incident beam voltage (40 keV) for AES which, when compared to our work [24], would have resulted in considerable electron-beam damage to high aspect ratio whisker structures.

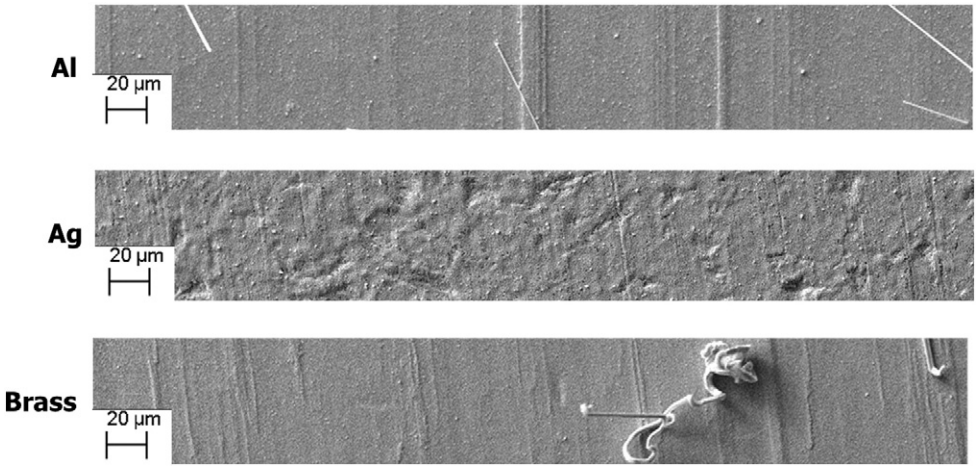


Fig. 8. Whisker images for thermal cycled specimens (74 cycles) with low %ΔCTE combinations.

AES has allowed us to determine several materials and surface properties of Sn whiskers; namely, surface composition, variations in surface composition along the whisker shaft, composition at the blunt end of the whisker shaft, the composition as a function of depth into the whisker, and whether the growth substrate (in this case, brass) constituents are observed either on the growing whisker surface or in the whisker bulk. A further question incapable of investigation with diffraction methods is whether the whisker has any unexpected concentrations of surface or bulk elements, long thought to be a key element in several models of whisker growth.

The Auger spectra shown in Fig. 5 show that, after Ar^+ sputter cleaning, the whisker is 100% Sn at all locations along the whisker shaft, at the growing blunt end of the shaft, and with depth (~1000 Å) into the side of the whisker. The "as received" Sn whisker surface shows the expected ~20 Å of native Sn oxide at all locations (known as the whisker "exoskeleton"). There was no evidence of oxygen or other impurity elements within the bulk of the whisker. That brass is not observed in the whisker supports the notion that whisker formation is a result of rapid, long-range material mass transport in the Sn film which affects stress (usually compressive) relief. In an elegant work involving tracer diffusion and SIMS in whisker platings, Woodrow [25] has shown that long range, lateral diffusion of isotopically labeled Sn can occur. It is remarkable that whiskers several hundred microns in length can grow from a ~0.6 μm thin film of Sn without seeing evidence of Cu or Zn from the brass substrate. The submicron thickness of the Sn film proved to be a key feature of this work because nearly all previous studies of Sn whiskering had employed Sn thicknesses of several microns, not tenths of microns. The submicron thickness of the Sn film highlights and clarifies the role of Sn supply and mass transport in whiskering phenomena, a crucial question in models of whisker formation. Subsequent experiments [26] using AES depth profiling and Rutherford backscattering spectroscopy (RBS) found a uniform "Sn swamp drain" (i.e., an overall Sn film thickness reduction) as high numbers of whiskers grow over long times from Sn films on semiconductor surfaces, supporting the observations of Woodrow. In rare cases, however, Sn whisker growth has been observed (by us and others) to consume Sn from a limited area immediately surrounding the whisker root. The dynamics of Sn movement to the whisker root remains to be fully worked out.

6. Whiskering at high relative humidity

Relative humidity has been shown to play a complicated role in whisker development. Some reports have claimed that moisture is not a contributing factor in whisker growth while others observe that whiskers form more readily under high humidity (≥85% RH) [27–29]. Humidity is thought to introduce stresses due to the diffusion of oxygen from the surface into the film [30]. High humidity then affects the thickness of the oxide film on the Sn leading to compressive stress [31]. High relative humidity is also thought to increase the rate of grain boundary

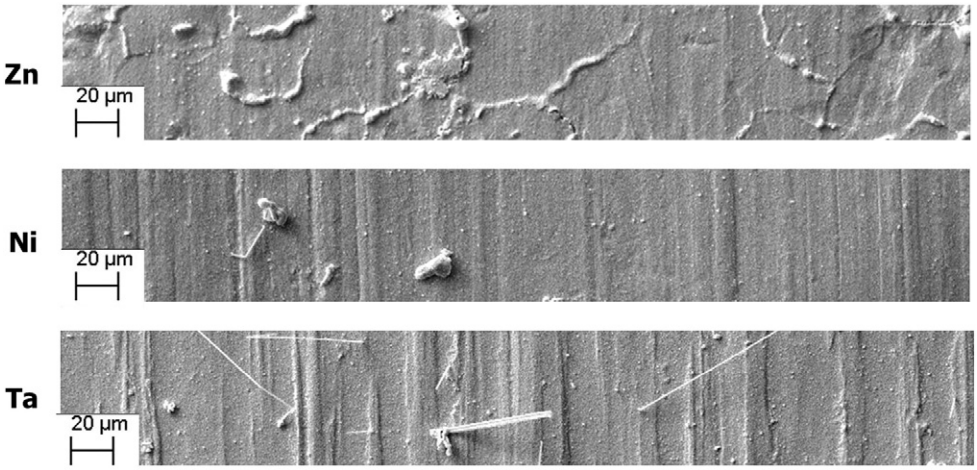


Fig. 9. Whisker images for thermal cycled specimens (74 cycles) with intermediate %ΔCTE combinations.

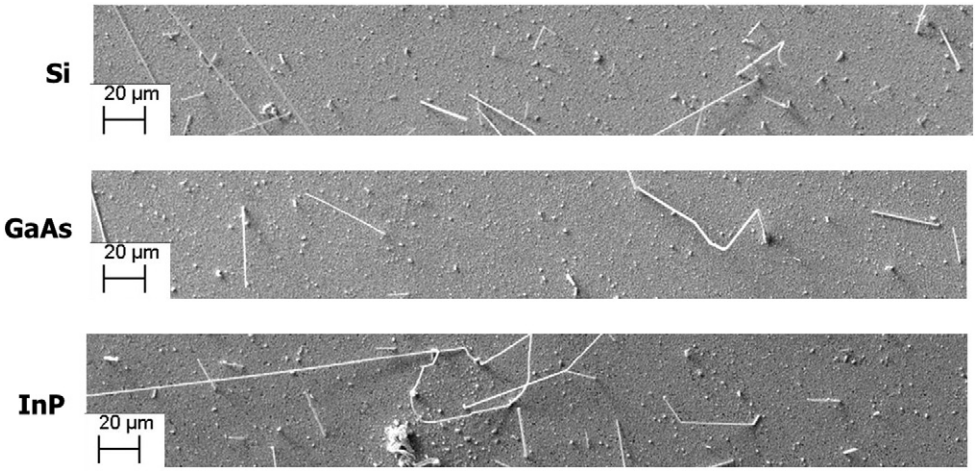


Fig. 10. Whisker images for thermal cycled specimens (74 cycles) with high %ΔCTE combinations.

or surface diffusion, and can also lead to corrosion, which introduces additional stress within the film. Corrosion-assisted whisker growth caused by water condensation during high-temperature humidity testing or by water droplet exposure has been observed [32]. Excessive localized surface corrosion leads to non-uniform oxide growth, which imposes differential stress on the Sn film. Whiskers have been found to nucleate in the corroded regions and continue to grow even after removal of the condensed moisture. It is clear from these works that humidity plays a significant role in whisker production. We report below the results of a highly controlled experiment on the effects of relative humidity on Sn whiskering.

Pure Sn films were sputter deposited on brass and Si substrates using a 99.999% pure Sn target. The thickness of the deposited films was 1500 Å, measured by stylus profilometry over a step edge of the deposit. The brass (Cu63/Zn36) substrates were commercial metal sheets which were cut into coupons of dimension 1 cm × 1 cm. To observe whisker growth within a reasonable time period, the brass coupon surfaces were electrochemically polished, since previous work showed enhanced whisker growth on smooth surfaces [33]. The Si substrates were (100) oriented, n-type commercial wafer specimens, snap cleaved to 1 cm × 1 cm dimensions. Si was chosen due to its atomically smooth surface and because Si and Sn do not create intermetallic compounds (IMC), which eliminates the film stress contribution due to IMC growth. The Sn films were sputtered at Ar gas pressures of 2–3 mT, producing intrinsic compressive stress in the films. Subsequently, the coupons were transferred to highly controlled environments containing the desired relative humidity. The humidity environments were created within air tight glass beakers with the coupons suspended over various saturated aqueous salt solutions (Table 3) used to maintain the calibrated relative humidity environments [34] at room temperature.

After one month, whisker growth was observed on every sample at every relative humidity. The 69.9% RH produced the most whiskers for both substrates at 29,080 (brass) and 14,409 whiskers/cm^2 (Si). The longest average whisker lengths were observed on the 75.5% RH samples (8.6 μm for brass and 3.7 μm for Si). The 75.5% RH Sn on brass specimen grew the longest whiskers, but it also produced the lowest whisker density (3668 whiskers/cm^2). The smallest whisker density observed for Sn on Si was at the lowest humidity, 33.1% RH (2620 whiskers/cm^2). Fig. 6 shows the whisker density as a function of time over the full range of humidity environments, 33–98% RH. The highest slope is for 85% RH, which agrees with previous studies concerning the effect of humidity on whiskering, where it was found that ~85–93% RH produces the higher whisker densities [35]. Whisker statistics after ~140 days shows an increase in whisker growth in all samples, with some Sn/Si samples exceeding 100,000 whiskers/cm^2. SEM photographs of the whiskers for the case of 85% RH are shown in Fig. 7.

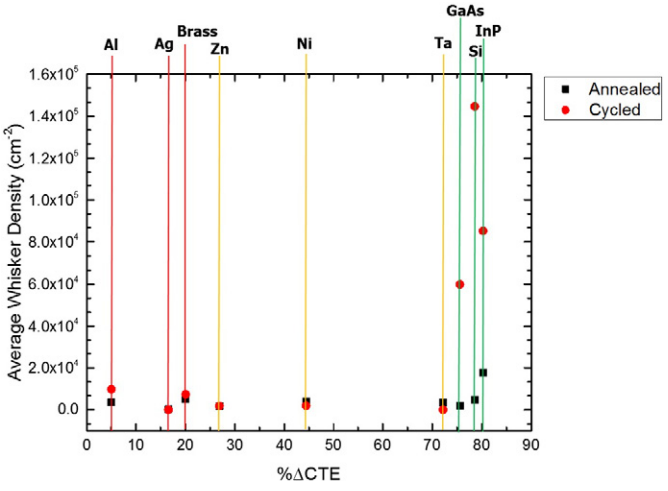


Fig. 11. Average whisker density for thermally cycled (−40 to 125 °C, 37 days, 74 cycles) and isothermally annealed (100 °C, 37 days) specimens.

7. Whisker growth utilizing high CTE Differences and thermal cycling

Systematic variations in the coefficient of thermal expansion (CTE) between Sn and the substrate provide a highly reliable and fast method to grow whiskers. The CTE effect can be enhanced by thermal cycling during whisker incubation. The principle traces to the freshman physics topic of the bimetallic strip, which bends convex or concave depending on the relative CTE of the bimetals. We noticed the dramatic effect of CTE on whiskering during early experiments designed to isolate the effect of IMC growth on whiskering. Much of the early work on whiskering was performed on brass substrates, which enhances

Table 3
ASTM saturated salt solutions used to create accurate relative humidity environments.

Saturated salt solutions	Calibrated relative humidity (RH)
Magnesium chloride	33.1 ± 0.2
Potassium carbonate	43.2 ± 0.4
Potassium iodide	69.9 ± 0.3
Sodium chloride	75.5 ± 0.2
Potassium chloride	85.1 ± 0.3
Potassium sulfate	97.6 ± 0.6

Table 4
Whisker density rankings for thin Sn films.

RED: comparative values

Generally higher whisker densities

Sn Film thickness (Å)	Substrate	Incubation environment[1]	Incubation time (days)	Whisker density (cm^{-2})	
1200	Ag	RT	118	289,019	CAVE lab record
2000				93,866	
5000	Si	Thermal cycling	37	150,000	
1500	Brass	33% RH	137	40,870	
		43% RH		25,806	
		70% RH		93,136	
		76% RH		81,740	
		85% RH		96,280	~ 7.5X the density of pure O_2 exposed Sn on brass
		98% RH		13,492	
	Si	33% RH		24,365	
		43% RH		22,662	
		70% RH		82,788	
		76% RH		110,296	
		85% RH		164,527	~ 4X the density of Sn on Si at RT
		98% RH		94,446	
1600	Ge	RT	116	39,167	
	Si			38,512	
	GaAs			27,378	
	InAs			23,710	~ 3X the density of pure O_2 exposed Sn on brass
	InP			21,221	
	Glass			1,703	
1400	Brass	Pure O_2 at 1 atm	113	12,881	
2000				3,821	
1500	Brass	RT	140	1,729	~ 9X the density of Sn on brass

[1]RT means normal (lab) room temperature and humidity conditions while RH means relative humidity (determined by calibrated vapor pressure solutions).

whiskering due to the unbalanced inter-diffusion for Sn/Cu couples, forming the intermetallic compound Cu_6Sn_5, which in turn develops stresses within the film/substrate region. As Cu diffuses into Sn, the molar volume increase for the combined Cu and Sn atoms in that region initially occupied only by the Sn atoms establishes a compressive stress state within the entire intermetallic region. The expansive forces generated by the formation of Cu_6Sn_5 intermetallic compound (IMC) are a fundamental driving force which presumably moves (diffuses) Sn atoms toward the film surface and, when conditions are correct, the whisker itself. While this theory summarizes and attempts to explain a vast amount of whisker information generated over decades of whisker observations on brass, we considered it an unnecessary distraction to our goal of generating fast whisker growth. There are much more effective whisker producing forces than the stress produced by the

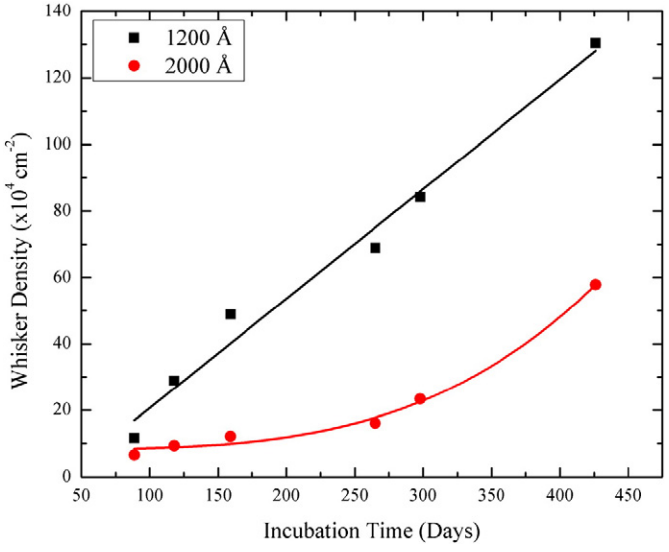


Fig. 12. Whisker density vs. incubation time for Sn/Ag for two thicknesses of Ag. Over the period of incubation, the average whisker length was 8.5 μm (2000 Å) and 9.0 μm (1200 Å).

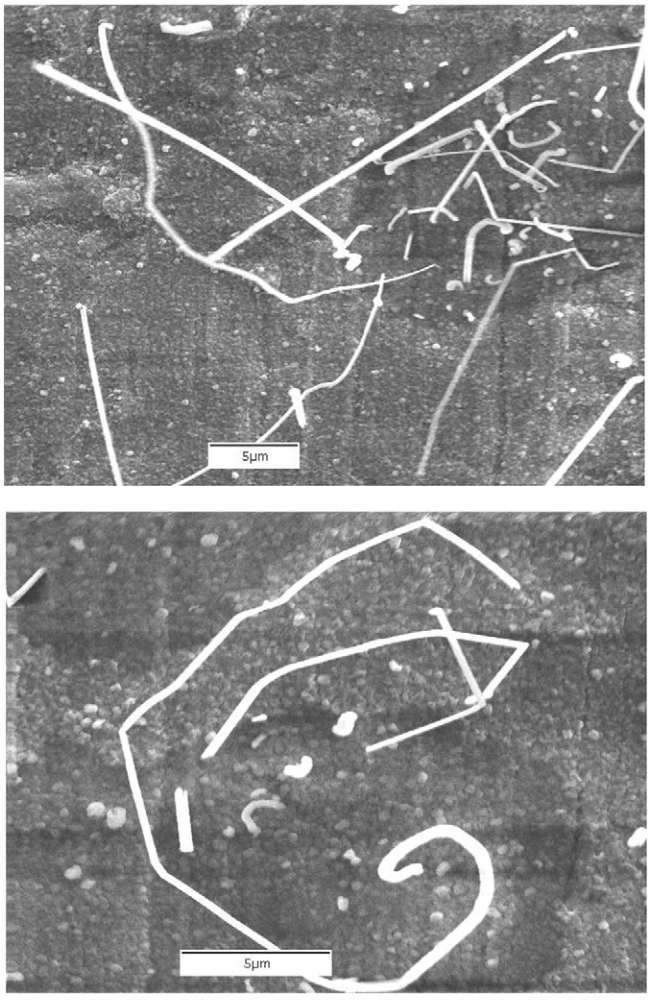


Fig. 13. SEM images of whisker growth from Sn films of 1200 Å on Ag substrates.

scalloped Cu-Sn IMC and, indeed, huge densities of whiskers can be generated on film systems (such as Sn on semiconductors) where *no* intermetallic compounds form.

To systematically characterize the effect of CTE on whiskering, we selected growth substrates having a range of CTE compared to Sn (Table 2). Substrates with CTE close in value to Sn ($0 < \%\Delta CTE < 25$) were Al, Ag, and brass; intermediate in value to Sn ($25 < \%\Delta CTE < 75$) were Zn, Ni, and Ta; and far in value to Sn ($75 < \%\Delta CTE < 100$) were semiconductors Si, GaAs, and InP. A thickness of 0.5 μm of sputtered Sn was deposited on each substrate under compressive stress conditions. A 500 Å Cr adhesion layer ensured good film adhesion during subsequent thermal cycling. After deposition, the samples were mounted, using Cu tape, onto Al trays for ease of transfer between the thermal chambers and the SEM. The thermal cycling range was −40 °C to 125 °C, with 2 h ramps and 4 h dwells, for a total of 12 h per cycle. A second, comparative set of specimens underwent isothermal annealing at 100 °C ± 5 °C. All samples were incubated for 37 days (74 cycles) before observation. The resulting whisker fields are shown in Figs. 8–10, with a summary plot of whisker density vs. %ΔCTE in Fig. 11.

The most impressive whisker fields are observed for the specimens having the largest %ΔCTE. The isothermally annealed samples had consistently lower whisker densities across all specimen combinations when compared to thermally cycled samples. This is intuitively reasonable, as constant temperature annealing would result in a lower average stress field in the film. Samples with a $\%\Delta CTE > 75\%$ resulted in *drastically* higher whisker densities (when cycled) compared with those with $\%\Delta CTE < 75\%$. In Fig. 11, there appears to be a critical activation (or

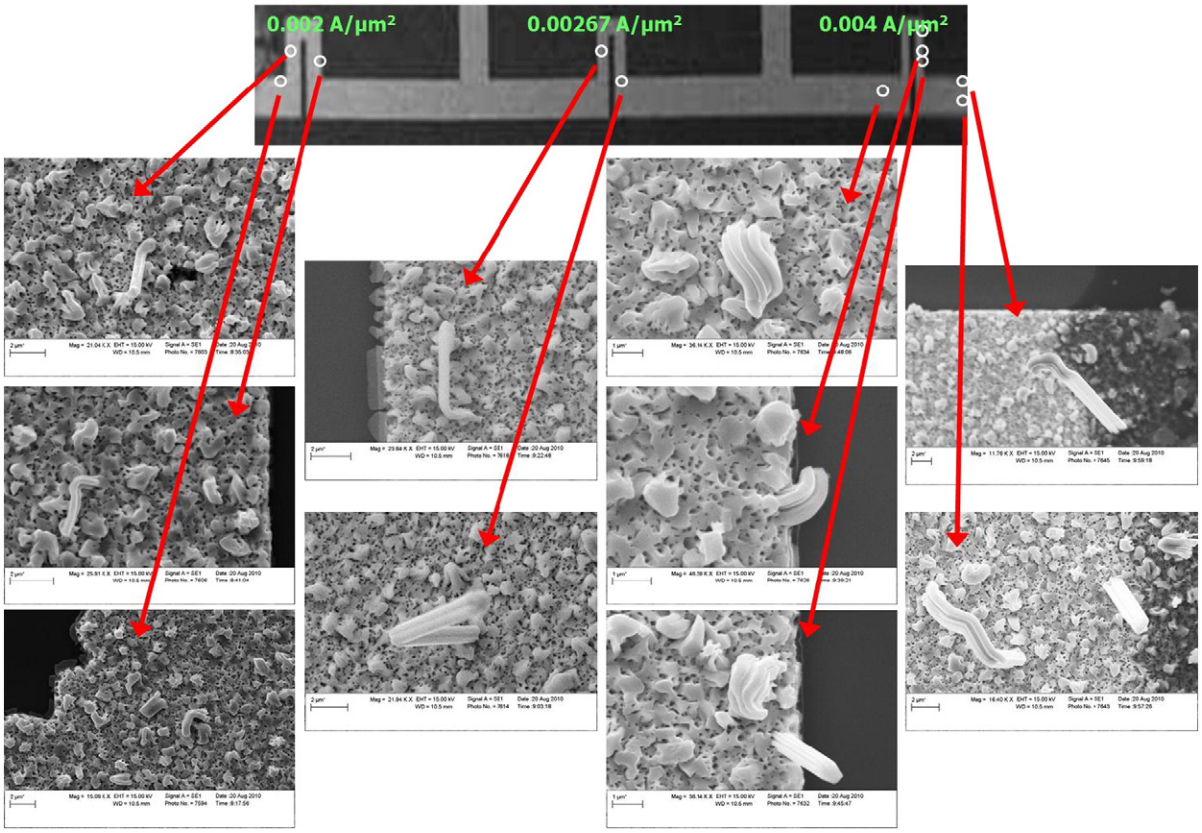


Fig. 14. SEM images of whiskers grown on the Sn pattern after 115 h of 0.2 A current stress.

nucleation) threshold CTE mismatch which "turns on" fast whisker growth when using semiconductors as substrates. The bottom line is that *very fast* Sn whisker growth occurs for film systems which are thermally cycled and have %ΔCTE > 75% mismatches. We have been using this technique for over a year as our primary method to grow fast, high density fields of Sn whiskers, largely using Si as the substrate.

8. Specialized methods of fast whisker growth

8.1. A spectacular case: whisker growth from Sn on Ag substrates

During an early search (unpublished) for fast whisker growing systems, experiments in our laboratory showed that the Sn/Ag combination was capable of producing extremely high (~0.25 million/cm^2) whisker densities (over three months of RT incubation). After several subsequent years of whisker work, the Sn/Ag still holds our internal lab record for prodigious whisker growth, for reasons we do not entirely understand. This subsection documents a recent attempt to quantify this incredible whisker producing system. Sn films were sputter deposited onto Ag substrates at thicknesses of 1200 and 2000 Å under compressive stress conditions. The Ag substrate was a commercial thin sheet of Ag foil cut into square pieces of dimensions 1 cm × 1 cm × 0.25 mm.

A plot of whisker density vs. time is shown in Fig. 12. Photographs of the whiskers are provided in Fig. 13. There is significant Sn whisker growth on both Sn thicknesses, but the thinner Sn film specimen (characteristically) has the higher whisker density. This is expected since the average macro-stress in thin films decrease with an increase in the film thickness. For example, the thinner 1200 Å Sn film produces a much greater number of whiskers (~116,000 whisker/cm^2) having a (slightly) longer average whisker length (10.7 μm). After 426 days of incubation, however, the 2000 Å Sn film grew the longest whiskers (11.5 μm). The longest whisker produced by the 2000 Å film was 394 μm long, showing again that submicron thin films of Sn can grow exceedingly long (hundreds of microns) whiskers. Equally, amazing is the extent of whisker growth on the 1200 Å Sn film on Ag, with over one million whiskers/cm^2. Sn on Ag is a remarkable whisker producer. At the end of one year of incubation, Sn on Ag continues to form whiskers at high rates, with no sign of a plateau or decrease in whisker growth.

8.2. Electrical bias enhancement of Sn whiskering

Since Sn atoms at room temperature are fairly mobile due to the low melting temperature (high homologous temperature at RT) of Sn, there is the possibility to be highly influenced by charge flow, resulting in electromigration of Sn atoms. This could lead to defects, hillocks and/or voids within the Sn films and accelerate whisker growth.

There has been limited work on the mechanism of Sn whisker growth driven by electrical force [36–38]. In 2004, S. H. Liu et al. [39] investigated Sn whisker growth in pure Sn due to the electromigration behavior in Sn. In that work, current densities of 7.5×10^4 and 1.5×10^5 A/cm^2 were driven through E-beam evaporated 5000 Å Sn deposited on 700 Å of Ti (used as the probing pads). Only one whisker grew due at 7.5×10^4 A/cm^2, which started growing after ~20 h of current flow. Voids were observed on the cathode and hillocks near the anode. The higher current density value produced multiple whiskers and hillocks. Whiskers ranged from 1 to 2 μm in diameter and grew as long as 200 μm after 260 h of current exposure. No whiskers were observed on the control test sample having zero current. Similar results were witnessed by Y. C. Hu et al. [40]. Electromigration was observed in fine lines of Sn foil about 30 μm in thickness, producing hillocks and voids due to 2×10^4 A/cm^2 of current density. Void and hillock formation occurred near the cathode edge after 500 h of exposure. Most of the studies identify a threshold current density when whisker growth increases dramatically. Our results generally agree.

Whisker growth due to electrical current differs from whiskers produced by mechanical stressing. Whisker growth by electrical currents appears to originate from the bombardment of electrons moving in the electric field from the cathode to the anode, pushing Sn atoms toward the anode. This creates voids on the cathode and results in compressive stress within the Sn film, which is relieved by whisker production throughout the film and hillocks near the anode end. One of our investigations on the effect of Sn electromigration on whisker growth was performed by passing current through a variety of sputter deposited, patterned Sn line thicknesses.

Sn was sputter deposited on a Si wafer using an Ar pressure of ~2–3 mT, creating compressive stress in a 1 μm Sn film. The Sn was sputtered through a mask pattern, produced using lithography. A current of 0.2 amps through the deposited lithographic features created current densities of 0.002, 0.00267, and 0.004 A/μm^2 (2×10^5, 2.67×10^5, and 4×10^5 A/cm^2). The 0.002 A/μm^2 region was near the cathode and the narrower 0.004 A/μm^2 region was near the anode. The current exposure was continuous except for brief pauses for whisker examination by Nomarski and SEM microscopy. The electrical current exposure was applied for a total of 115 h.

Fig. 14 shows that more whiskers grew with higher current densities and longer current stress times. No whiskers were produced until 10 h of exposure was reached, and then whiskers were produced in the two highest current density sections. The basic conclusion is that exposing a 1 μm Sn film pattern to 0.2 A of current produced whiskers in hours instead of weeks or months. After only 10 h of steady 0.2 A current, a small number of whiskers are found on the 0.004 and 0.00267 A/μm^2 sections of the Sn pattern. Whisker production occurs on the 0.002 A/μm^2 section after another 10 h (total of 20 h) of current exposure. After 20 h of current exposure the 0.002 A/μm^2 section begins to form hillocks, with slight amounts of increased whiskering in all sections. From 20 h to 80 h of current exposure no dramatic changes are observed; only in the 0.002 A/μm^2 section is a small amount of additional voids forming. After 115 h of current exposure, multiple voids form in the 0.002 A/μm^2 section but little whiskering. An increase in hillocks was found in the 0.002 and 0.00267 A/μm^2 sections together with the onset of voids is the 0.004 A/μm^2 section. While the whiskers formed by electrical stress do not have the classic, high aspect ratio shape that whiskers characteristically display on sputtered Sn films in the absence of electromigration, they form in hours and could be useful in whisker applications.

9. Conclusion

The understanding of whisker phenomena is substantially improved by the ability to grow reliable, dense fields of high-aspect Sn whiskers in weeks rather than months and years. This has allowed us to make demonstrable, systematic progress in identifying the key variables involved with Sn whiskering. Whereas many whisker studies are carried out over years, we are able to answer important, specific, experimental questions on whiskers in a three-month timeframe. The result has been a large "in-house" database of well-characterized whisker specimens that provide a key body of experimental information to compare to evolving models of whisker incubation and growth. Table 4 provides a summary ranking of whisker growth statistics over a broad array of studies we have done over the last few years. There are several distinctive characteristics of our approach to whisker studies: 1) We use a reliable, clean method of growing whiskers in a reasonable (weeks) timeframe by using magnetron sputtering techniques rather than electrochemical deposition; 2) We are able to easily synthesize tailor-made films with known "dialed-in" degrees of initial, intrinsic thin film stress (tensile, none, compressive) to investigate and exploit the role of net film stress; 3) We make fast progress. Due to the reduced time of whisker production, it is rare that our whisker studies exceed six months. We attempt to answer a limited set of questions, or even one key question on whiskers, rather than managing a multi-coupon, multi-variable, long-term experiment; 4) We study "laboratory" created whisker specimens with high aspect ratios, as opposed to archival, industrial, and/or anecdotal whisker specimens; and, 5) We study whisker growth from very thin films (~ 0.2 μm) compared to most whisker studies. This allows us to grow whiskers faster and has enabled us to examine several key questions on whiskers, such as the issue of lateral Sn diffusion, mass balance as whiskers grow, and the origin of the "Sn feedstock" necessary for whisker growth.

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