Chapter 2
Film/Substrate Effects on Whisker Growth

I think physicists are the Peter Pans of the human race. They never grow up and they keep their curiosity.

I. I. Rabi.

2.1 The Influence of Film Thickness on Sn Whiskering

The thickness of the deposited film has been thought to effect whisker growth. Since is it commonly agreed that compressive stress plays an important role in whisker formation, thicker Sn layers ($\sim$7 μm or greater) are thought to distribute the film stress over a larger volume, resulting in lower net stress values within the film.

Oberndorff et al. [1] studied electroplated Sn films deposited on typical lead-frame materials with varying thicknesses between 1.5 and 15 μm. In order to influence the whisker growth, several heat treatments and storage conditions were used. It was observed that increasing film thicknesses produced shorter whiskers. The whisker incubation time was also longer for thicker layers and ambient room temperature/humidity samples grew the longest whiskers. All whiskers from Sn film thicknesses of $\sim$5–10 μm were <50 μm long (most suggest Sn film thicknesses of $\sim$7 μm or greater). However, thicker films cannot be considered as a countermeasure to prevent whisker growth since eventually whiskers will still grow. In a second, related study, Oberndorff et al. [2] observed no whisker growth on electroplated Sn films >11.6 μm in thickness incubated under ambient room temperature/humidity after $\sim$325 days.

Do the trends observed by Oberndorff hold for films <2 μm? Can one expect similar results for sputtered Sn films? Whence, we have investigated the role of film thickness on Sn whisker growth for sputtered Sn on electro-polished brass over a thin Sn film regime ranging from 375–20,000 Å (0.0375–2 μm). Two classes of brass substrates were utilized for this experiment. One class was brass "out of the box," meaning a purchased, unpolished specimen supplied in sheet form. The other class was brass that had been commercially electropolished. In both cases, the starting material was a commercial [3] thin sheet of muntz brass having composition Cu (63 wt %) and Zn (37 wt %), cut into several square pieces each of approximate dimensions 1 × 1 × 0.25 cm.

Sn films were deposited on the brass by using a standard magnetron sputtering system operating at an Ar gas pressure of 2–3 mTorr. The Sn target was 99.99998 % pure (Kurt Lesker). The Sn film thicknesses investigated were 375,

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750, 1,125, 1,500 Å, along with slightly thicker films of 3,000, 6,000, 12,000, and 20,000 Å. All deposited film thicknesses were measured using a stylus profilometer on a sputter-deposited Sn on Si wafer under identical deposition conditions. This procedure was necessary due to the difficulty in accurately measuring film thicknesses on (rough) brass.

In early thin film work using a similar magnetron sputter deposition system, Thornton and Hoffman [4] determined the critical pressures for the compressive-to-tensile stress transition in thin films as a function of atomic mass. This plot, shown in Fig. 2.1, was used to determine the sputtering pressures necessary to produce thin Sn films under states of compression, tension, and zero stress. All Sn films thicknesses were deposited under a compressive stress state. After deposition, the samples were stored at ambient pressure and room temperature for several weeks until long, high aspect ratio Sn whiskers were generated. A Cambridge Stereoscan 200 scanning electron microscope (SEM) enabled observation of the whisker growth in time.

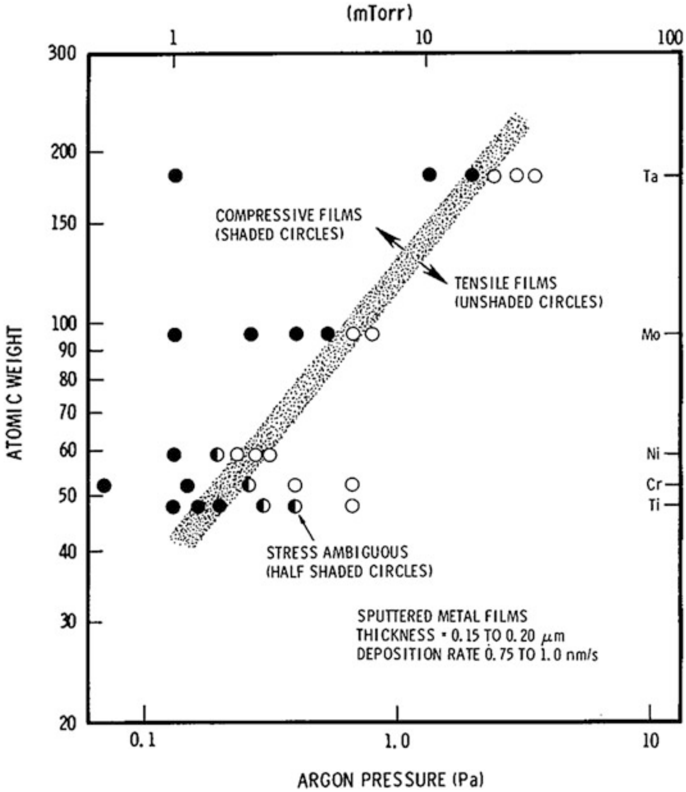


Fig. 2.1 Atomic mass versus working Ar pressure dependence for compressive and tensile sputter deposited metal films. Reprinted with permission from [4]. Copyright (1977), American Vacuum Society

Table 2.1 Whisker statistics on ultra-thin Sn films after 140 days of incubation

Sn film thickness (Å)	Polished (P) Unpolished (U)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
375	P	5,868	73.5	112.4	14
	U	0	0	0	0
750	P	6,758	36.8	74.5	5
	U	1,048	16.5	16.4	5
1,125	P	6,339	18.7	20.5	5
	U	1,938	7.6	4.4	7
1,500	P	1,729	14.2	23.7	5
	U	0	0	0	0

Table 2.2 Whisker statistics on ultra-thin Sn films after 211 days of incubation

Sn film thickness (Å)	Polished (P) Unpolished (U)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
375	P	8,225	61.6	110.2	10
	U	1,048	8.8	10.8	4
750	P	8,749	22.1	39.0	6
	U	4,768	9.0	12.8	2
1,125	P	10,216	17.3	22.1	4
	U	3,824	4.8	3.5	2
1,500	P	3,563	6.5	10.4	4
	U	419	4.1	1.5	3

2.1.1 Ultra-Thin Film Whiskering

After a few months of incubation in ambient room temperature/room humidity (RT/RH) the ultra-thin Sn films (375, 750, 1,125, and 1,500 Å) on brass were observed in the SEM, with corresponding whisker statistics shown in Table 2.1. It is evident that rough brass substrates produce fewer whiskers than polished brass substrates. After less than 5 months of incubation all ultra-thin Sn films on polished brass produced whiskers densities between 5,000 and 7,000 cm^{-2}, with the exception of the 1,500 Å thickness with a whisker density of only ~1,700 cm^{-2}. Tables 2.2 and 2.3 show the whisker statistics after further incubation periods. It is evident that all samples (polished and unpolished substrates) are producing more whiskers over time. After ~1.4 years of incubation, the 1,125 Å film is producing the most whiskers (~26,000 whiskers/cm^2) and the 1,500 Å film is producing the fewest whiskers (~9,300 whiskers/cm^2). Figure 2.2 shows representative SEM photographs of the whiskers formed on the various ultra-thin Sn films.

In Fig. 2.3, the whisker growth rate is plotted, which allows us to determine if we are approaching an asymptotic whisker density. Observing no plateau in the whisker density versus time plot suggests there is still a sufficient amount of Sn

Table 2.3 Whisker statistics on ultra-thin Sn films after 470 days of incubation

Sn film thickness (Å)	Polished (P) Unpolished (U)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
375	P	13,885	45.5	87.9	3
	U	2,620	5.4	5.1	3
750	P	19,780	10.3	25.4	2
	U	12,837	5.6	6.0	2
1,125	P	26,199	13.0	29.8	4
	U	9,956	3.6	2.5	2
1,500	P	9,301	4.3	6.7	2
	U	655	2.6	0.5	3

feedstock left on the surface. By the use of Auger electron spectroscopy (AES) depth profiling it is possible to measure the thickness of the Sn film left after whisker growth. The depth profile was performed by successive manual sputter/spectra cycles to carefully observe when the brass substrate was reached for an accurate thickness. AES spectra in Fig. 2.4 shows the existence of Cu and Zn at a depth of 300 Å below the free Sn surface after 211 days of incubation for the 1,125 Å film, suggesting Sn film depletion during whisker growth and/or increasing Cu-Sn IMC growth during the incubation period, but still enough feedstock left to continue producing whiskers. The AES data was acquired from four evenly spaced positions over the surface of the sample, all giving the same results, which implies that the film is consuming Sn uniformly over the surface. The AES spectra in Fig. 2.5 on the 750 Å sample shows a Sn thickness of 25 Å after 360 days of incubation, which also appears to be depleting the Sn feedstock uniformly.

Since we (1) observe uniform film thickness decreases during the whisker growth period and (2) do not observing local Sn depletion immediately surrounding the whisker root, a reasonable conclusion is that the Sn used to grow whiskers originates from a large range of proximity on the film. Woodruff [5] also reported data using tracer elements and secondary ion mass spectroscopy (SIMS) showing that Sn can migrate over large distances within the film. That we see the Sn pond draining uniformly additionally supports the notion of long-range Sn migration during whisker growth. Further, we generally find that, for the case of ultra-thin Sn films, thicker Sn films produce higher whisker densities for polished brass substrates (the exception is the thickest, 1,500 Å film), while for Sn on unpolished brass, the thinner films produce the highest whisker densities (the exception is the thinnest, 375 Å film). Sn film thicknesses between 750 and 1,125 Å produce the highest whisker densities for polished and unpolished brass substrates. We also find that polished substrates and thinner films tend to grow the longest whiskers. This is in agreement with Oberndorff et al. [1].

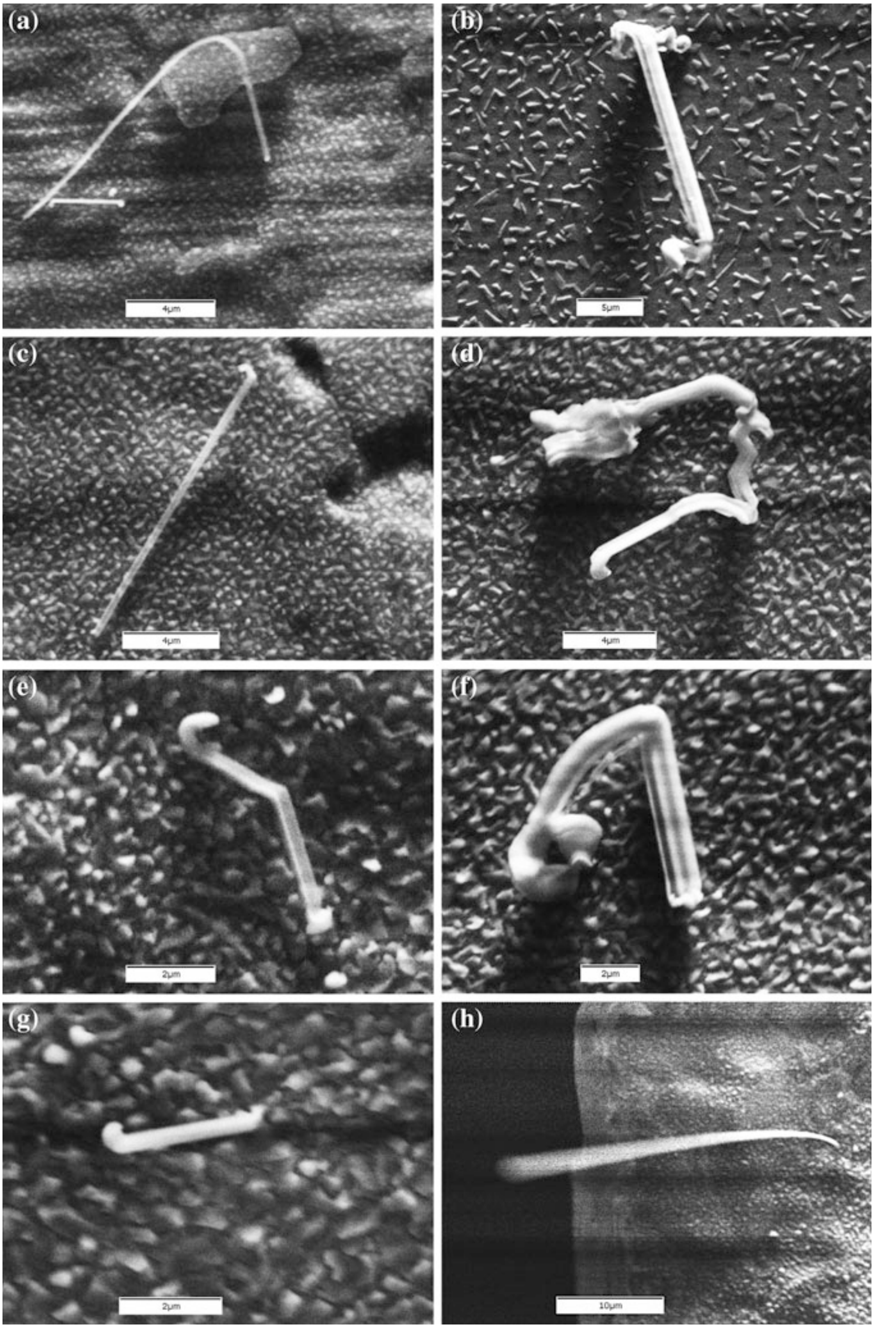


Fig. 2.2 SEM whisker images from ultra-thin Sn films on polished (*P*) and unpolished (*UP*) brass **a** 357 Å on UP, **b** 357 Å on P, **c** 750 Å on UP, **d** 750 Å on P, **e** 1,125 Å on UP, **f** 1,125 Å on P, **g** 1,500 Å on UP, and **h** 1,500 Å on P

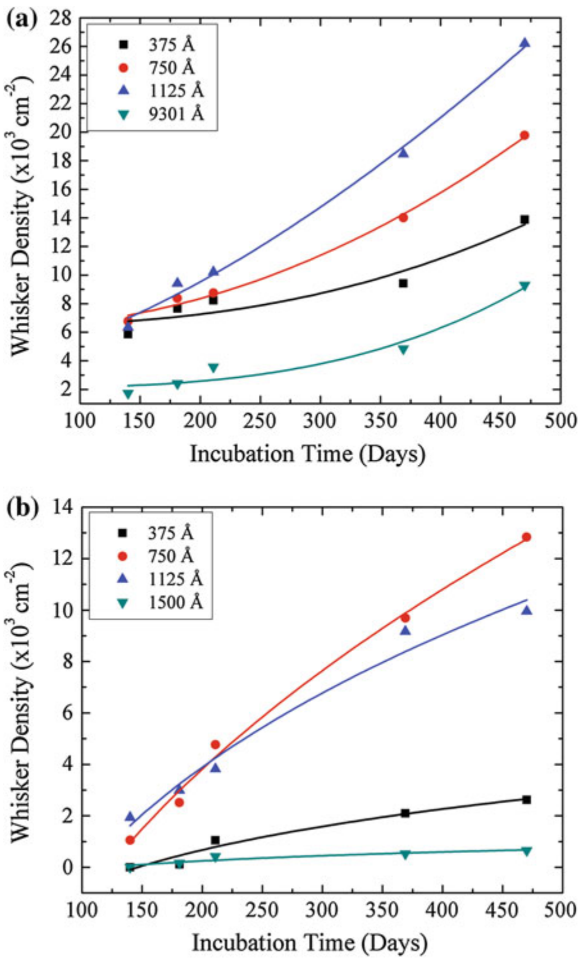


Fig. 2.3 Whisker density versus incubation time for Sn on **a** polished brass, and **b** unpolished brass

2.1.2 Thicker Sn Film Whiskering

In this experiment, Sn films were sputter deposited on electro-polished brass (only) with thicknesses of 0.3, 0.6, 1.2, and 2.0 μm under compressive stress conditions. The samples were incubated at ambient room temperature/humidity and periodically observed in the SEM for whisker growth. The whisker statistics after ~4 months of incubation is shown in Table 2.4. At this point in time, the highest whisker density (~11,800/cm^2) is found on the 1.2 μm Sn film. However, the lowest whisker producer (6,000 Å film, ~5,600 whiskers/cm^2) grew the longest average whiskers (~44 μm) compared to the thicker 1.2 and 2 μm films, with average whisker lengths around 13 μm.

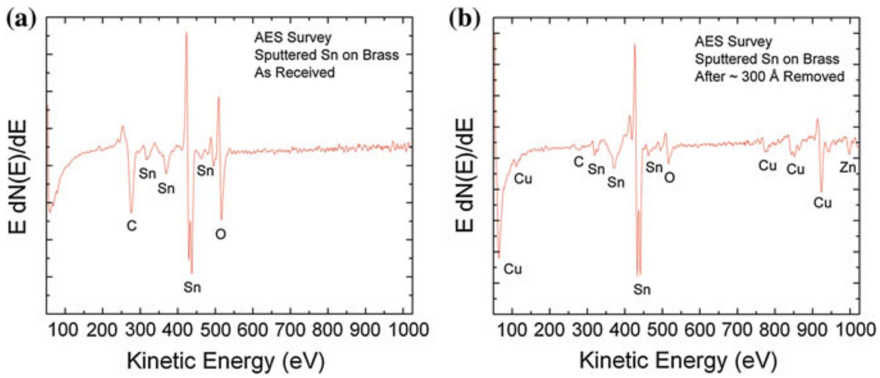


Fig. 2.4 AES survey taken after 211 days of incubation for the case of 1,125 Å Sn on polished brass **a** as received, and **b** after ~300 Å removed

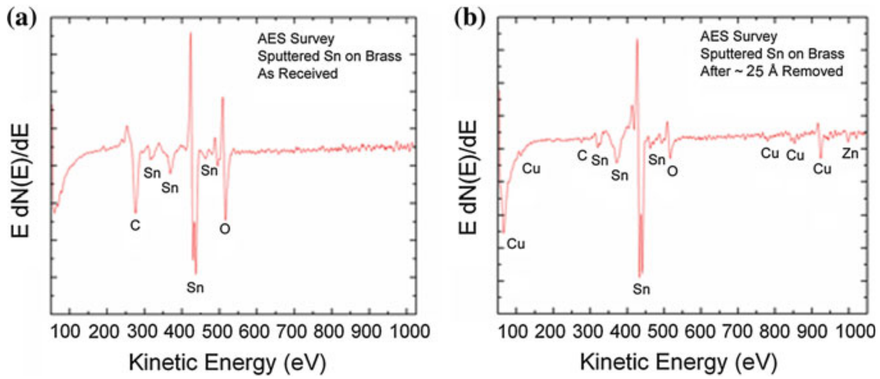


Fig. 2.5 AES survey taken after 360 days of incubation for the case of 750 Å Sn on polished brass **a** as received, and **b** after ~25 Å removed

Table 2.4 Whisker statistics on various Sn film thicknesses after 123 days of incubation

Sn film thickness (μm)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
0.3	7,531	21.5	43.2	5
0.6	5,566	43.5	69.6	6
1.2	11,788	13.5	13.4	4
2.0	8,404	13.2	12.0	5

Tables 2.5 and 2.6 show the whisker growth after an extended incubation period, up to ~1.2 years. The highest whisker density is found on the thinnest 0.3 μm Sn film (~33,300 whiskers/cm^2). The 0.6 μm film is producing the lowest whisker density (~19,000 whiskers/cm^2); however, it is still growing the longest whiskers, with an average whisker length of ~21 μm, which is about twice the

Table 2.5 Whisker Statistics on Various Sn Film Thicknesses after 268 Days of Incubation

Sn film thickness (μm)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
0.3	20,959	11.0	30.3	3
0.6	9,060	33.4	92.2	3
1.2	20,522	10.1	15.8	4
2.0	16,047	9.1	10.7	4

Table 2.6 Whisker statistics on various Sn film thicknesses after 434 days of incubation

Sn film thickness (μm)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
0.3	33,272	7.5	24.4	3
0.6	18,994	20.6	78.6	4
1.2	32,093	9.6	10.0	5
2.0	27,378	10.1	13.2	5

average whisker length of the next longest whisker producing specimen (the 2.0 μm film, producing an average whisker length of ~10 μm). SEM images of some representative whiskers from these specimens are shown in Fig. 2.6.

The whisker growth rate for each sample is shown in Fig. 2.7. All samples are continuing to produce whiskers with no sign of a whisker density plateau. This is corroborated by AES data taken in Fig. 2.8 on the 0.3 μm film, the thinnest of these films, which shows there is plenty of Sn feedstock remaining (existence of Cu and Zn at a depth of 625 Å below the free Sn surface after 125 days of incubation and a depth of 500 Å below the Sn surface after 165 days). The depth profiles were recorded at four widely spaced positions on the surface with similar results, which again indicates that the "Sn pond" is draining uniformly as whiskers incubate and grow.

Figure 2.9 compares the whisker density and whisker length versus film thickness for the full range of Sn film thicknesses. On polished brass, we find that thicker films produce higher whisker densities, with an optimum of film thickness of 3,000 Å. The case of polished brass is different from a wide variety of other whisker growth experiments reported in this thesis, which characteristically show that thinner films produce more whiskers. It is not clear at the moment what is causing this variation, except to note that brass suffers from the complication of the Su-Cu intermetallic compounds at the interface which, for the thin films studied here, may be dominating the interfacial mechanics. From Fig. 2.9c, the thinnest, 375 Å film produced the longest whiskers (one whisker up to 577 μm long) and the thickest (12,000 and 20,000 Å) films grew the shortest (with one exception in the 1,500 Å Sn film). This trend largely follows the results seen by Oberndorff et al. [1], where thinner films grew longer whiskers and the thicker films produced shorter whiskers.

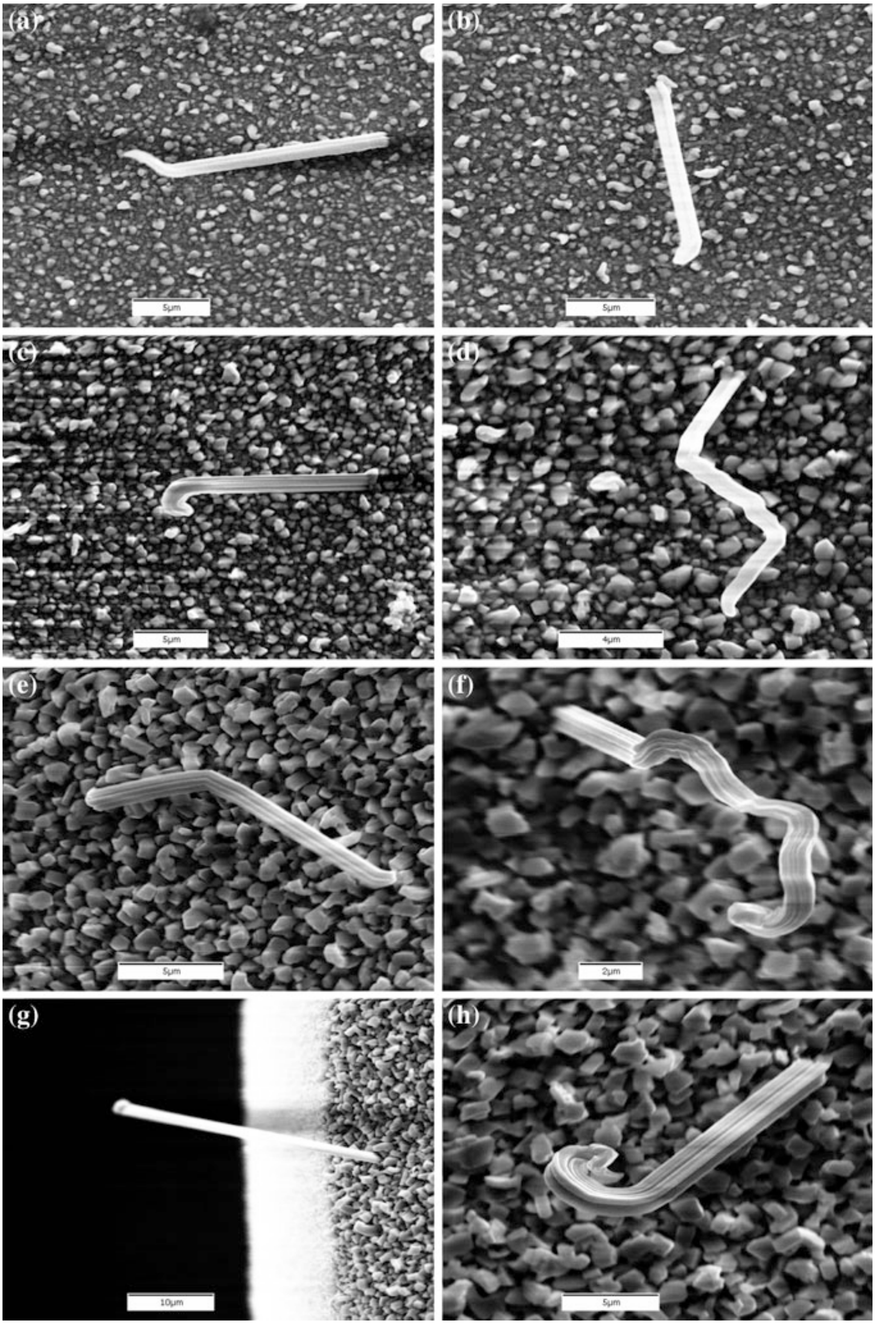


Fig. 2.6 SEM whisker images from sputtered Sn film thicknesses **a, b** 3,000 Å, **c, d** 6,000 Å, **e, f** 12,000 Å, and **g, h** 20,000 Å on polished brass

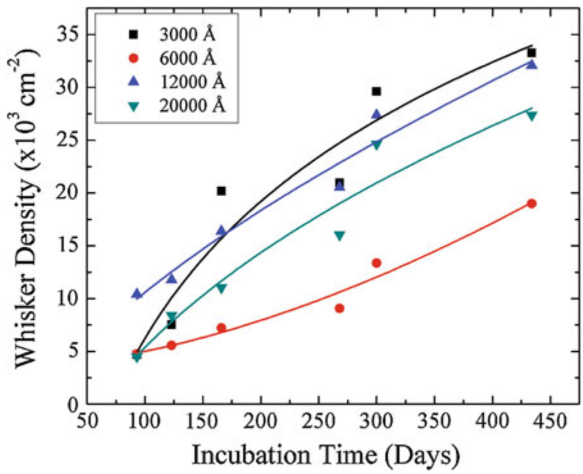


Fig. 2.7 Whisker density versus incubation time for sputtered Sn on polished brass

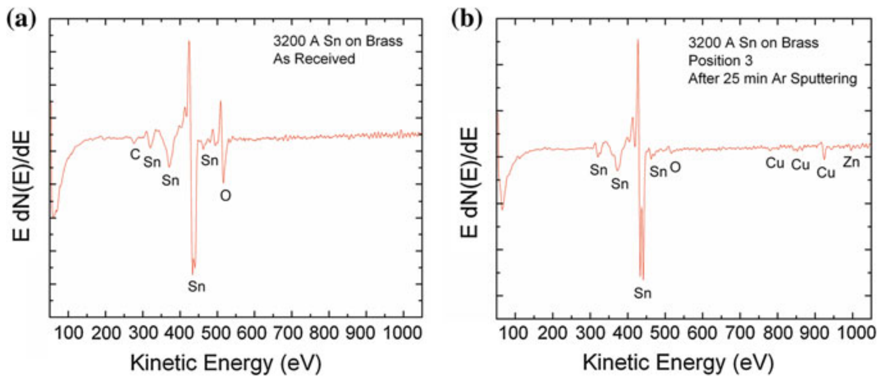


Fig. 2.8 AES survey taken after 125 days of incubation for 0.3 μm Å Sn on polished brass **a** as received, and **b** after ~25 min of Ar^+ sputtering

2.2 Whisker Growth from Patterned Arrays of Deposited Sn

By use of high lateral resolution AES measurements on Sn whiskers grown on brass, it has been shown by Bozack et al. [6] that a whisker is 100 % Sn at all locations along the whisker shaft, including the growing blunt end of the shaft and with depth (~1,000 Å) into the whisker, with no observation of brass pull-up in the whisker. Since Sn whiskers are composed entirely of Sn, with no indication that the deposition substrate is pulled up into the whisker, an important question to address is the origin of the Sn in the whisker, known as the feedstock issue. We addressed this issue above in our earliest whisker experiments and report further nuances on it here.

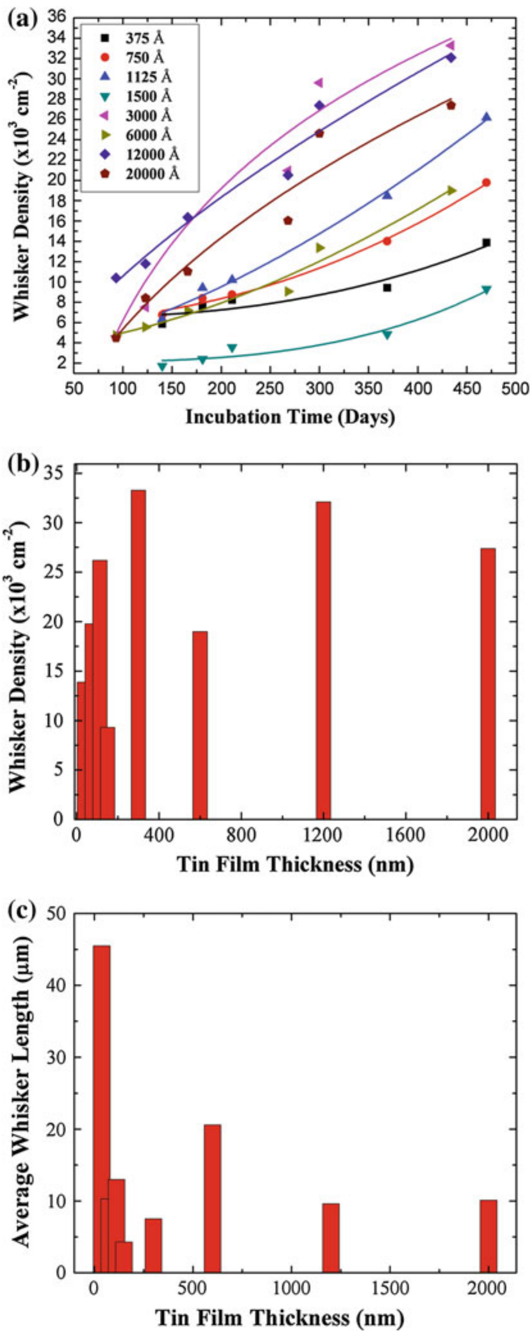


Fig. 2.9 Comparison of whisker growth versus film thicknesses on polished brass **a** whisker density versus incubation time, **b** whisker density versus Sn film thickness, and **c** average whisker length versus Sn film thickness (up to ∼450 days)

The fact that brass was not observed in the whisker shaft supports the notion that whisker formation is accompanied by material mass transport through interfaces and grain boundaries which causes stress (usually compressive) relief. Direct evidence of lateral diffusion of Sn during whisker growth was reported in elegant tracer experiments performed by Woodrow [5]. The existence of substantial lateral mass transport during whisker growth is also supported by one of the most remarkable aspects of whisker growth; namely, that high aspect ratio Sn whiskers $\sim$100–500 μm in length containing no brass can be grown from **submicron** thin films of Sn. In this section, we explore this fact in more detail by asking whether a minimum amount of deposited Sn is necessary to produce whisker growth. We have done this by studying Sn whisker growth on ultra-thin (<2,000 Å) *patterned arrays* of Sn on brass, where it may be possible to observe a maximum growth length and, in addition, determine if the surrounding Sn in the array element is *used up* during the whisker growth. The ideal result we anticipated was that, over a sufficiently long growth period, the patterned array of Sn would *disappear* as the surrounding Sn was consumed during whisker growth. Further, by studying Sn whisker growth on variously sized square and circular areas of Sn, we surmised that it may be possible to directly observe lateral surface diffusion by examining the region between the deposited features, which would be initially devoid of Sn. Last, since whisker growth is connected to high stress, we anticipated that we may observe more whiskers at the corners of rectangular shaped array elements than for circular array elements. While the final results of this experiment proved to be disappointing, one valuable observation gleaned was that optimum whisker growth seems to be favored by a large lateral supply of Sn.

Two deposition substrates were selected for the experiment. The substrates were polished and unpolished brass of composition Cu (63 wt %) and Zn (37 wt %). The patterned Sn films were deposited by sputtering through open apertures in various grid structures [7, 8] laid atop the growth substrate. The grids are commonly used in transmission electron microscopy for calibration purposes. The Sn deposition was carried out at a chamber Ar gas pressure of 2–3 mTorr, which produces compressive stress in the Sn films. The deposited Sn thicknesses were 1,200 and 2,000 Å for Sn on brass. Due to the difficulty in measuring film thicknesses on (comparatively rough) brass, the deposited film thicknesses were measured using stylus profilometry on a Sn on Si wafer sputtered under identical conditions. After deposition, the samples were stored at ambient room temperature/humidity and monitored periodically for whisker growth. The grid structures are shown in Fig. 2.10 with details in Table 2.7. Images of the resulting deposited Sn patterns are shown in Fig. 2.11. The colored boxed regions in Fig. 2.11 indicate the specimen location where whisker statistics were gathered.

Table 2.8 shows the whisker statistics after a few months of incubation for the Sn on brass case. Most patterned areas show some signs of whiskering within the first $\sim$105 days. The G75 screen (largest patterned area) has produced the most whiskers and, on the opposite end, the smallest patterns (CF-4/2-2C and CF-1/1-2C) show no whisker growth. At this incubation time, no firm conclusions can be made apropos to whisker density versus substrate roughness. However, with

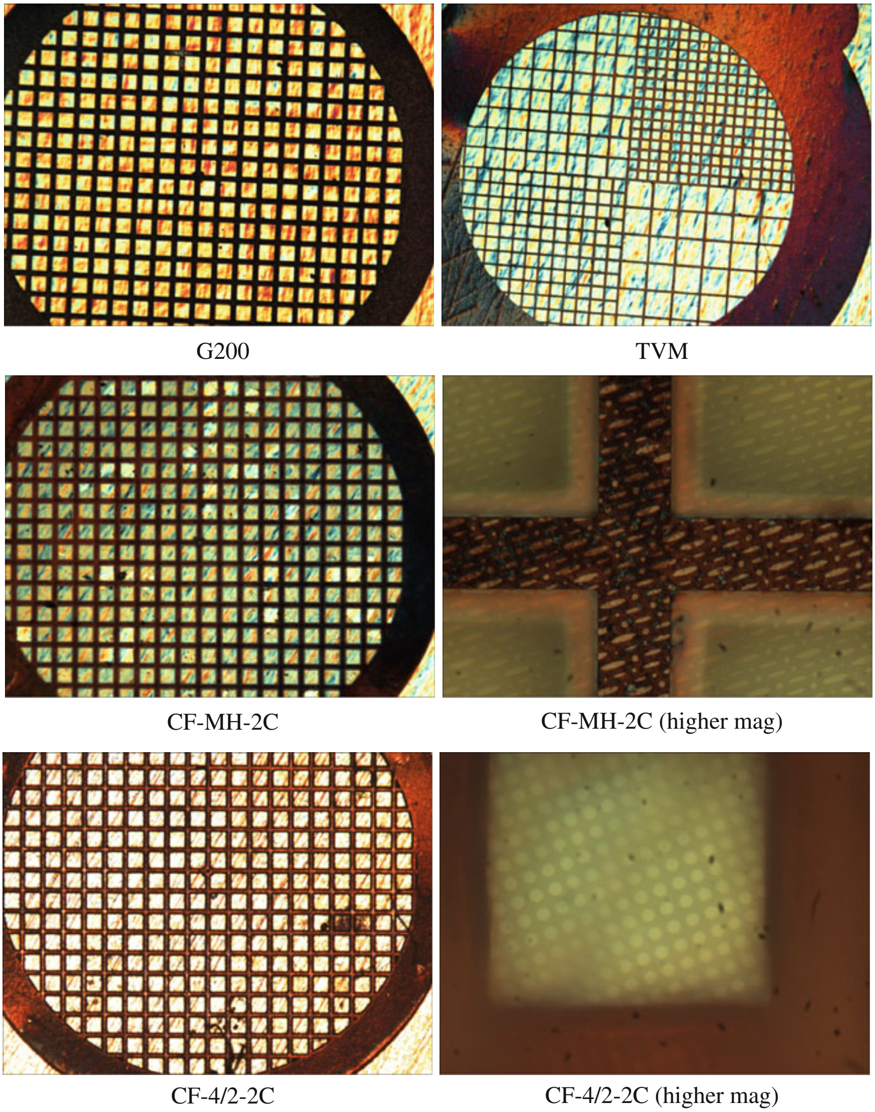


Fig. 2.10 Normarski (optical) microscope images of patterned *grid structures* used for patterned Sn deposition

further incubation up to ~415 days (Table 2.9) the polished brass produces more whiskers than the unpolished brass in nearly all cases. This agrees with our previous results. Generally, we see that the larger the patterned area, the greater the whisker growth, with the largest Sn features, G75 and G100, producing the greatest number of whiskers. The smallest, CF-4/2-2C and CF-1/1-2C, patterns are still not producing whiskers after almost 1.2 years of incubation.

Table 2.7 Pattern dimensions for grid structures

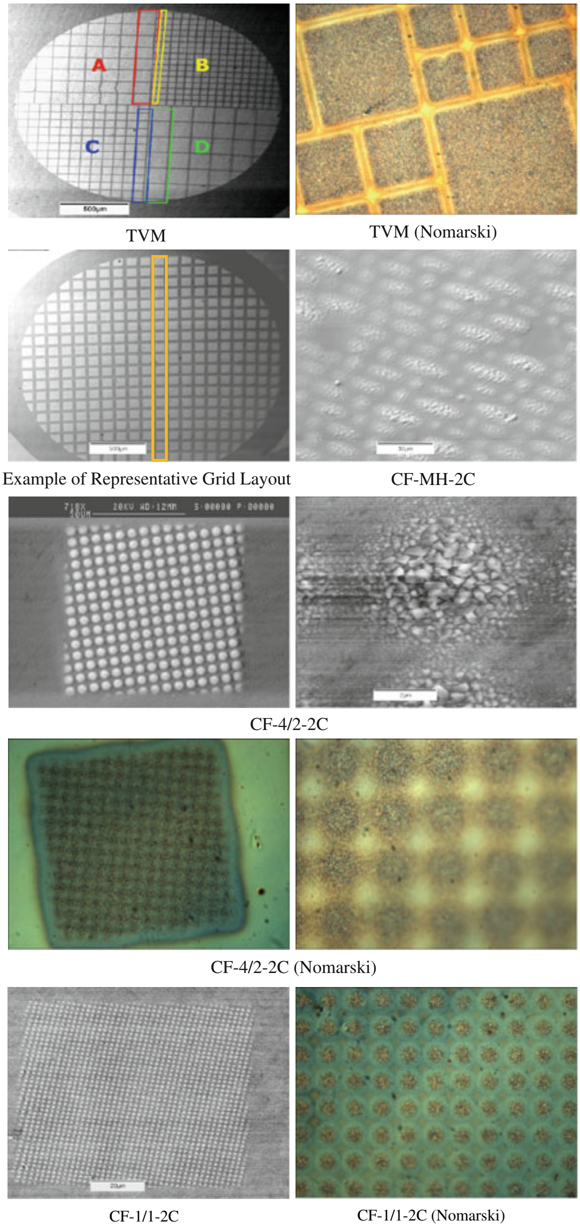
Fixed aperture grids		Corresponding pattern size
G75		285 × 285 μm^2, w/55 μm spacing
G100		205 × 205 μm^2, w/45 μm spacing
G150		125 × 125 μm^2, w/40 μm spacing
G200		90 × 90 μm^2, w/35 μm spacing
CF-MH-2C		Multi hope, ellipse, and spacing
CF-4/2-2C		4 μm hole, w/2 μm spacing
CF-1/1-2C		1 μm hole, w/1 μm spacing
TVM: combination grids	A	153 × 153 μm^2, w/13 μm spacing
	B	113 × 113 μm^2, w/12 μm spacing
	C	73 × 73 μm^2, w/10 μm spacing
	D	54 × 54 μm^2, w/8 μm spacing

In general, the overall trend in whisker growth on patterned Sn features is *significantly* lower than the whisker numbers on un-patterned (~1 cm^2) Sn films deposited under similar stress conditions and incubation times. The very low whisker numbers from the smallest deposited features leads to the supposition that a minimum size/volume of Sn may be necessary for optimum whisker growth. Table 2.10 shows the whisker growth after ~2.6 years, where there is an increase in whisker numbers from some of the larger Sn features. However, even after over 2.6 years, whisker growth is *pitifully low* from the majority of Sn patterns and *zero* on the smallest features. Further, we are not seeing any depletion zones around the whisker roots or within the patterned Sn features, nor are we observing (at least from microscopy images) any gross lateral Sn diffusion between the Sn features. Figure 2.12 shows some representative whiskers growing from the various patterns of Sn.

2.3 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. After several subsequent years, the Sn/Ag still holds our internal lab record for prodigious whisker growth. This subsection documents a more recent attempt to quantify this incredible whisker system. Sn films were deposited onto Ag substrates at thicknesses of 1,200 and 2,000 Å under compressive stress conditions. The Ag substrate was a commercial thin sheet of Ag foil [3] cut into square pieces of dimensions 1 cm × 1 cm × 0.25 mm.

Fig. 2.11 SEM and Nomarski images of deposited Sn patterns



Whisker data after 3 months of incubation is given in Table 2.11. There is significant Sn whisker growth on both specimen thicknesses, but the thinner Sn film specimen (characteristically) has the higher whisker density. For example, the thinner 1,200 Å Sn film produces a much greater number of whiskers (~116,000

Table 2.8 Whisker statistics for Sn on brass patterns after ~105 days of incubation

Pattern	Polished (P) Unpolished (U)	Total # of whiskers	Average whisker length (μm)	Standard deviation (μm)	Mode
G75	P	54	5.1	4.7	3
	U	28	4.6	2.3	5
G100	P	9	2.4	0.5	2
	U	1	4	N/A	N/A
G150	P	8	3	1.4	2
	U	0	N/A	N/A	N/A
G200	P	7	2	0	2
	U	8	2.5	0.76	2
CF-MH-2C	P	0	N/A	N/A	N/A
	U	3	2	0.51	2
CF-4/2-2C	P	0	N/A	N/A	N/A
	U	0	N/A	N/A	N/A
CF-1/1-2C	P	0	N/A	N/A	N/A
	U	0	N/A	N/A	N/A
TVM	P(A)	9	3.1	1.4	2
	P(B)	4	2.25	0.5	2
	P(C)	3	2.7	0.6	3
	P(D)	6	2.5	0.8	2
	U(A)	12	6.3	9.8	3
	U(B)	1	2	N/A	N/A
	U(C)	4	2.75	0.5	3
	U(D)	6	2.83	0.75	3

whisker/cm^2) having a (slightly) longer average whisker length (10.7 μm). After 426 days of incubation (Table 2.12), however, the 2,000 Å Sn film grew the longest whiskers (11.5 μm). The longest whisker produced by the 2,000 Å film was 394 μm long, showing again that submicron thin films of Sn can grow exceedingly long (hundreds of microns) whiskers. And then, equally amazing, is the extent of whisker growth on the 1,200 Å Sn film on Ag, with over one million whiskers/cm^2 (see Fig. 2.13). Sn on Ag is a remarkable whisker producer!.

A plot of whisker density versus time is shown in Fig. 2.14. Even at the end of one year, Sn on Ag continues to form whiskers at high rates, with no sign of a plateau or even a decrease in whisker growth.

Such a fast growing whisker system offers an optimum test bed to investigate how the "Sn swamp" is draining during whisker growth. Whence, AES depth profiling was carried out on the 1,200 Å film. Figure 2.15 shows the results of drilling ~600 Å (12 min of AES depth profiling at ~50 Å/min) into the Sn film after 120 days of incubation. The height of the Ag Auger feature at this depth in the Sn film shows that roughly half of the Sn remains after 4 months of whisker growth. By repeating the measurement at four widely spaced areas on the specimen (Fig. 2.16) similar results suggest once again that the Sn feedstock is draining

Table 2.9 Whisker statistics for Sn on brass patterns after ~ 415 days of incubation

Pattern	Polished (P) Unpolished (U)	Total # of whiskers	Average whisker length (μm)	Standard deviation (μm)	Mode
G75	P	154	6.9	6.5	3
	U	35	3.9	1.7	4
G100	P	83	3.6	3.4	2
	U	7	2.4	0.5	2
G150	P	58	3.0	1.4	2
	U	1	2	N/A	N/A
G200	P	14	3.0	1.0	3
	U	2	3.0	1.4	N/A
CF-MH-2C	P	4	4.0	2.8	2
	U	8	2	0	2
CF-4/2-2C	P	0	N/A	N/A	N/A
	U	0	N/A	N/A	N/A
CF-1/1-2C	P	0	N/A	N/A	N/A
	U	0	N/A	N/A	N/A
TVM	P(A)	21	5.8	4.1	2
	P(B)	10	2.5	1.0	2
	P(C)	15	3	1.3	2
	P(D)	27	3.3	1.9	2
	U(A)	25	3.0	1.7	2
	U(B)	4	2	N/A	2
	U(C)	10	2.8	1.0	2
	U(D)	18	3.2	1.2	3

uniformly during whisker growth. We will show data later in the thesis which investigates the feedstock drain idea more carefully using Rutherford backscattering spectroscopy.

2.4 Sn/Substrate Combinations Which Eliminate the Influence of Intermetallic Formation

Many studies of Sn whiskers have emphasized the role of intermetallic compound formation at the tin-substrate interface, which is believed to induce a high compressive stress state in the film [9, 10]. The increased compressive stress in high tin plated components (on Cu) is thought to be a major contributor to Sn whisker growth. The goal of the work in this subsection is to characterize whisker growth from sputtered Sn films where intermetallic compounds (IMC) are **absent** and compare to sputtered Sn films where IMC's are known to exist. A corollary purpose of our studies was to see whether differences in whisker production *between* the chosen substrates could be attributed to coefficient of thermal

Table 2.10 Whisker statistics for Sn on brass patterns after ~955 days of incubation

Pattern	Polished (P) Unpolished (U)	Total # of whiskers	Average whisker length (μm)	Standard deviation (μm)	Mode
G75	P	358	6.2	6.8	3
	U	38	2.7	1.0	2
G100	P	94	4.0	3.8	2
	U	7	2	0	2
G150	P	61	3.4	2.2	2
	U	1	2	N/A	N/A
G200	P	51	3.2	1.7	2
	U	4	2.3	0.5	2
CF-MH-2C	P	11	3.0	1.2	3
	U	8	2	0	2
CF-4/2-2C	P	0	N/A	N/A	N/A
	U	0	N/A	N/A	N/A
CF-1/1-2C	P	0	N/A	N/A	N/A
	U	0	N/A	N/A	N/A
TVM	P(A)	76	4.6	3.9	2
	P(B)	36	2.8	1.5	2
	P(C)	47	3.5	2.5	2
	P(D)	85	4.6	5.0	2
	U(A)	27	2.5	1.3	2
	U(B)	5	2	0	2
	U(C)	11	2.3	0.6	2
	U(D)	21	2.4	0.8	2

expansion (CTE) mismatches, which invariably exist when different materials are mated as a bimetallic strip. While CTE effects on whisker growth are expected to be small for material systems maintained at isothermal temperatures, it is nonetheless useful to be aware of possible effects owing to CTE variations between film and substrate. For the record, Table 2.13 shows a substantial CTE mismatch between Sn and the various substrates in this study (Si, Ge, GaAs, InP, InAs, and glass), but very little mismatch between the substrates *themselves*.

A pure Sn sputter target (99.999 %, Kurt Lesker Co) was used to deposit 1,600 Å Sn films on a variety of semiconductor and insulator surfaces (Si, Ge, GaAs, InP, InAs, and glass) in a magnetron sputtering system. The film thickness was verified by stylus profilometry over a step edge in the deposit. The semiconductor and glass substrates were commercial, wafer thickness specimens. The Sn films were sputtered at argon pressures of 2–3 mTorr which produced an intrinsic compressive stress in the Sn films [13]. The samples were then incubated under ambient room temperature/humidity (RT/RH) conditions followed by periodic whisker counts for many months using a Cambridge scanning electron microscope (SEM). After 4 months (120 days) of incubation and whisker growth, the Sn films were examined using Auger electron spectroscopy (AES) and

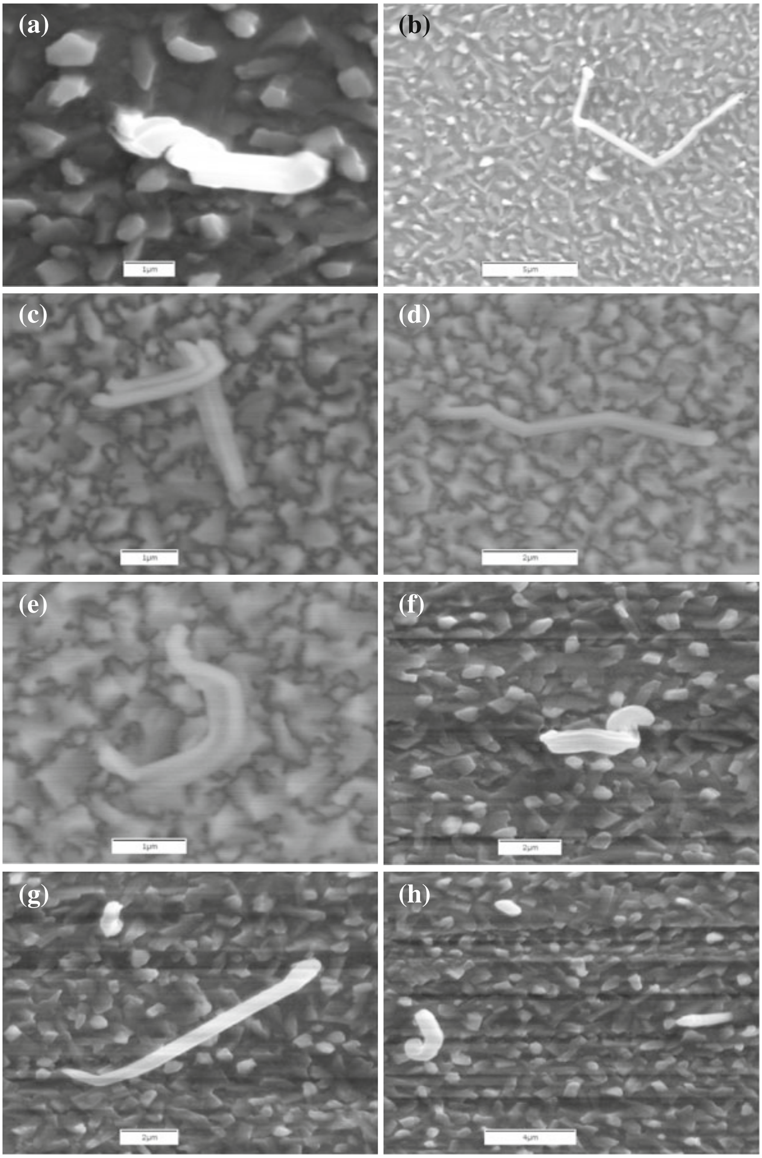


Fig. 2.12 SEM images of various whiskers from polished (*P*) and unpolished (*UP*) brass substrates with Sn features **a** G75 UP, **b** G75 P, **c** G100 P, **d** G150 P, **e** G200 P, **f** TMV-A UP, **g** TMV-B UP, and **h** TMV-C UP screens

Table 2.11 Whisker statistics for sputtered Sn on Ag after ~90 days of incubation

Sn film thickness (Å)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
1,200	116,132	10.7	15.2	4
2,000	66,143	8.2	6.8	3

Table 2.12 Whisker statistics for sputtered Sn on Ag after ~425 days of incubation

Sn film thickness (Å)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
1,200	1,303,505	8.4	12.6	3
2,000	578,989	11.5	24.9	3

Rutherford back scattering (RBS) techniques in order to measure the Sn film thickness as a function of growth time.

After ~50 days of incubation in ambient room temperature/humidity conditions, the growth of Sn whiskers on the various film combinations was recorded by SEM. The whisker densities were determined by manually counting whiskers over ten equal representative areas (~275 × 275 μm) on the surface. Table 2.14 shows the whisker growth statistics. All Sn film/substrate combinations produced whiskers after 54 days of incubation. Si and Ge substrates yielded the largest whisker densities of 15,195 and 19,911 whiskers/cm^2 respectively. Si and Ge also produced the longest average whisker lengths, with 6.6 μm for Si and 7.5 μm for Ge. The Sn on glass substrate shows the lowest density of whiskers (262 whiskers/cm^2) along with the shortest average whisker length of 2.5 μm.

Table 2.15 shows the whisker statistics after another 2 months of incubation (total of 116 days). The Sn on Si and Ge specimens are still producing the largest whisker densities, surpassing 35,000 whiskers/cm^2; however, Sn on InAs, GaAs, and InP are producing the longest average whisker lengths (InAs leads with an average whisker length of 8.3 μm). Further, during the additional 2 months of incubation, Sn on InAs, GaAs, and InP combinations show sudden increases in whisker growth, resulting with 21,000–28,000 whiskers/cm^2. In contrast, Sn on glass still lags in whisker density (1,703 whiskers/cm^2) with an average whisker length (2.5 μm) compared to the other semiconductor and insulator substrates. Though high whisker densities are produced over the various Sn/substrate combinations, the average whisker lengths for all the samples are only in the single digits. A representative sample of the high aspect ratio whiskers produced on the various films is shown in Fig. 2.17. Figure 2.18 illustrates the whisker density versus incubation time for each sample.

It is interesting to see in Table 2.16 that the substrates yield markedly different whisker densities over the first 54 days of incubation but, between 54 and 116 days, the *increases* in whisker density are *similar* (glass is a notable exception). This means that the various surfaces initially produce quite different whisker densities but then begin to produce similar whisker densities, ranging between

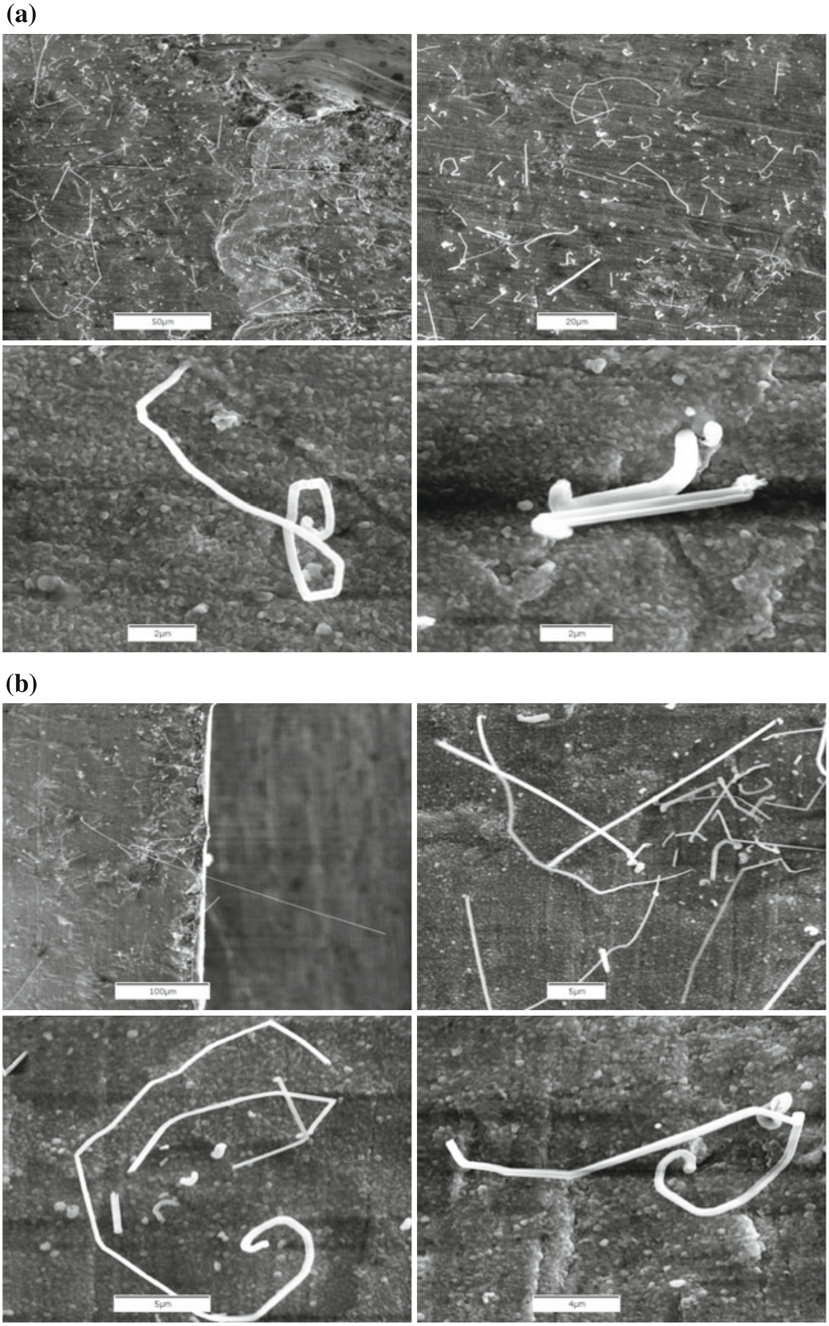


Fig. 2.13 SEM images of whisker growth from Sn films of **a** 1,200 Å, and **b** 2,000 Å on Ag substrates

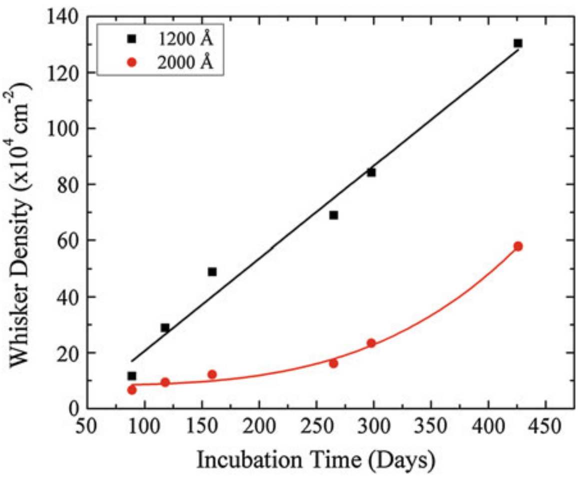


Fig. 2.14 Whisker density versus incubation time for Sn on Ag

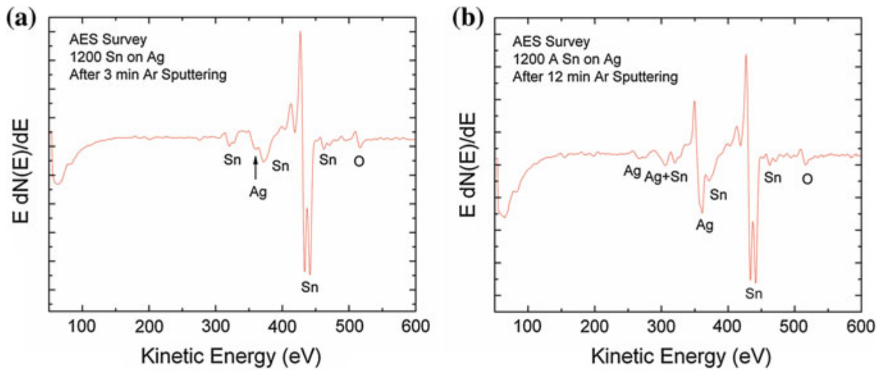


Fig. 2.15 AES survey taken after 120 days of incubation on 1,200 Å during sputter depth profiling of **a** 3 min, and **b** 12 min

18,000 and 23,000 whiskers/cm^2. This may suggest a critical nucleation step or activated process operating after the initial incubation period. There have been several activated growth mechanisms in complex whisker-producing thin film systems suggested, ranging from critical strain relief levels, recrystallization to form oblique grain boundaries, oxygen diffusion kinetics into grain boundaries, stress-assisted Cu and Sn diffusion, the work necessary to puncture the tin oxide surface, creep and plastic deformation levels, and so on.

Rutherford backscattering spectroscopy (RBS) was used to observe any noticeable change in the Sn film thickness during whisker incubation and growth on the various semiconductor/insulator substrates. In RBS, an incident 2 MeV α-particle beam is scattered from the film and film/substrate interface. The energy

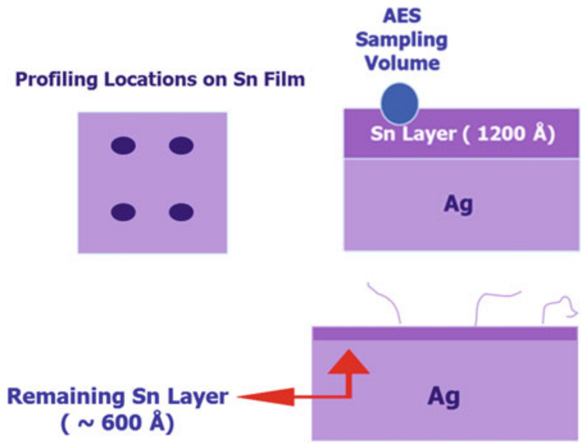


Fig. 2.16 Cartoon of AES depth profiling into the 1,200 Å Sn film on Ag

Table 2.13 Comparison of linear coefficients of thermal expansion

Substrate	CTE[a] (10^{-6} K^{-1})	ΔCTE[b]	%ΔCTE[b]
Sn	23.4	0	0
Si	5.1	18.3	78.2
Glass (Pyrex)	4	19.4	82.9
InP	4.6	18.8	80.3
GaAs	5.7	17.7	75.6
InAs	4.5	18.9	80.8
Ge	6.1	17.3	73.9

[a] Refs. [11, 12]; [b] Compared to Sn

loss by the α-particles during scattering from the front and back surface of the Sn film (the a, b distance in the RBS spectrum in Fig. 2.19) yields the Sn film thickness.

Figure 2.20 shows the RBS-determined Sn film thickness versus incubation time for three substrates. For each sample the RBS data was taken at widely spaced positions, producing similar results. While it is difficult to measure such small incremental variations (~100 Å) in film thickness with most analytical techniques

Table 2.14 Whisker statistics after 54 days of incubation

Substrates (1,600 Å Sn film)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode[a]
Si	15,195	6.6	9.1	2
Glass	262	2.5	0.7	N/A
InAs	655	6.0	3.5	N/A
GaAs	7,074	4.2	3.8	2
InP	3,668	3.3	1.6	2
Ge	19,911	7.5	7.6	2

[a] Mode is defined as the most frequently observed whisker length

Table 2.15 Whisker statistics after 116 days of incubation

Substrates (1,600 Å Sn film)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
Si	38,512	6.5	7.9	2
Glass	1,703	2.5	0.7	2
InAs	23,710	8.3	5.8	6
GaAs	27,378	6.9	6.5	2
InP	21,221	6.9	6.2	2
Ge	39,167	6.6	6.8	2

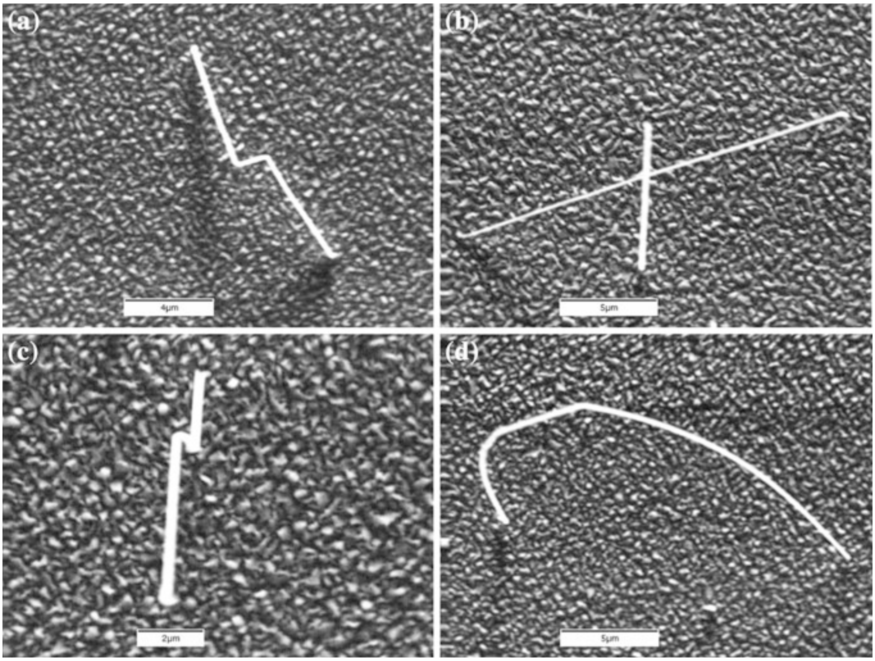


Fig. 2.17 Representative whisker morphologies produced on various Sn/semiconductor combinations **a** Sn on GaAs at 4270X, **b** Sn on InP at 3760X, **c** Sn on Si at 6350X, and **d** Sn on GaAs at 3760X

(including RBS), there is a general trend toward decreasing Sn thickness with incubation time. Notice further that, in some samples, there is an apparent increase in Sn film thickness at the end of the incubation time. We believe this is attributable to two factors; first, that a non-uniform sputtered film thickness may exist over the broad extent of our specimen sizes (1 × 1 cm); and, second, that the RBS particle beam "sees" the whiskers formed at the top of the surface, which effectively makes the film "look" thicker. The second explanation is more likely since we have only rarely observed non-uniform film deposits in our sputtering system.

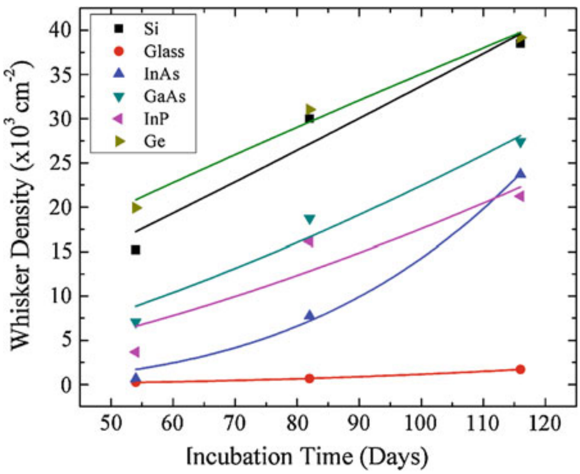


Fig. 2.18 Plots of whisker density versus incubation time for the 1,600 Å Sn film on various semiconductors/insulators exposed to RT/RH conditions

Table 2.16 Whisker density change between 54 and 116 days of incubation

Substrates (1,600 Å Sn film)	Whisker density change (cm^{-2}) (116–54 days)
Si	23,317
Glass	1,441
InAs	23,055
GaAs	20,304
InP	17,553
Ge	19,256

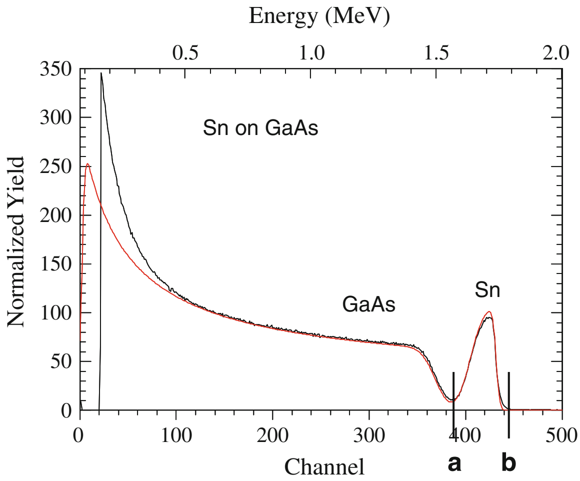


Fig. 2.19 Sn films thickness determination on GaAs measured by RBS

The RBS thickness measurement is difficult because of the large lateral size of the specimens needed for RBS. What is needed optimally is a large amount of whisker growth over ~120 days of incubation to significantly "thin" the Sn feedstock. Values of ~100–150 Å of film depletion for the films push the depth resolution of RBS for this class of interfaces. RBS works best on semiconductor film stacks which approach atomic flatness. Sputtered tin, on the other hand, has a very rough top surface which limits the accuracy of thickness measurements in RBS.

In Fig. 2.20, the RBS results indicate that the Sn on GaAs sample has depleted ~100 Å of Sn film during ~120 days of whisker growth. Is the amount of film diminution consistent with the expected mass balance as the depleted film ends up as Sn whiskers? Table 2.17 shows several calculated mass balance possibilities for whisker density and length assuming that 100 Å of Sn is depleted due to whisker growth. The numbers in **bold** correspond to the whisker density and average length values measured here for the Sn on GaAs sample. The numbers correlate favorably to the RBS-derived ~100 Å of Sn film consumption reported in Fig. 2.20. For the case of InP, the RBS measured ~150 Å decrease in film thickness corresponds to an average whisker length of ~10 μm for the measured whisker density of 21,221 whiskers/cm^2 while the measured average whisker length was ~7 μm.

It is best to view the mass conservation calculations as a "sanity check" of the RBS results. They turned out better than expected given the approximations cited above and limited statistics when manually counting and measuring whiskers in an SEM. One other major approximation is that we typically do not measure the thickness of the whiskers, which varies slightly from surface-to-surface and whisker-to-whisker. The whisker radius used for all mass conservation estimates was 1.5 microns, which is a reasonable average.

Finally, Auger depth profiling was used to ascertain the film composition with depth after 130 days of incubation (Fig. 2.21). The Sn on Si and Sn on Ge samples (largest whisker producers) were selected for this purpose. Two observations are noteworthy; first, the AES derived Sn film thickness (1,600 Å) agrees well with the deposited film thickness measured by both RBS, stylus profilometry, and through familiarity with the Sn sputter deposition rates generated by our magnetron sputter system; second, there is evidence of diffusion between the Sn and Si and Ge during the incubation period at ambient room temperature/humidity. This was surprising, as we expected minimal diffusion and a sharper interface under room temperature conditions. The depth resolution of our AES depth profiling system is insufficient to detect the ~100 Å of film depletion observed by RBS.

In conclusion, it is clear that Sn whiskers grow readily on thin, sputter-deposited Sn films on semiconductor and insulator substrates under internal compressive film stress conditions where intermetallic layers are absent. The fact that Sn on semiconductor surfaces grows copious amounts of whiskers is consistent with our earlier work on surface roughness, which showed that smoother surfaces grow more whiskers [14]. Semiconductor surfaces are some of the smoothest surfaces that can be technologically manufactured.

For the case of Sn on semiconductors/insulators, the highest whisker density after 116 days of incubation occurs for the Si and Ge substrates (38,512 and

Fig. 2.20 Representative plots of the Sn film thickness versus incubation time for the substrates *Si*, *InP* and *GaAs*, determined by RBS

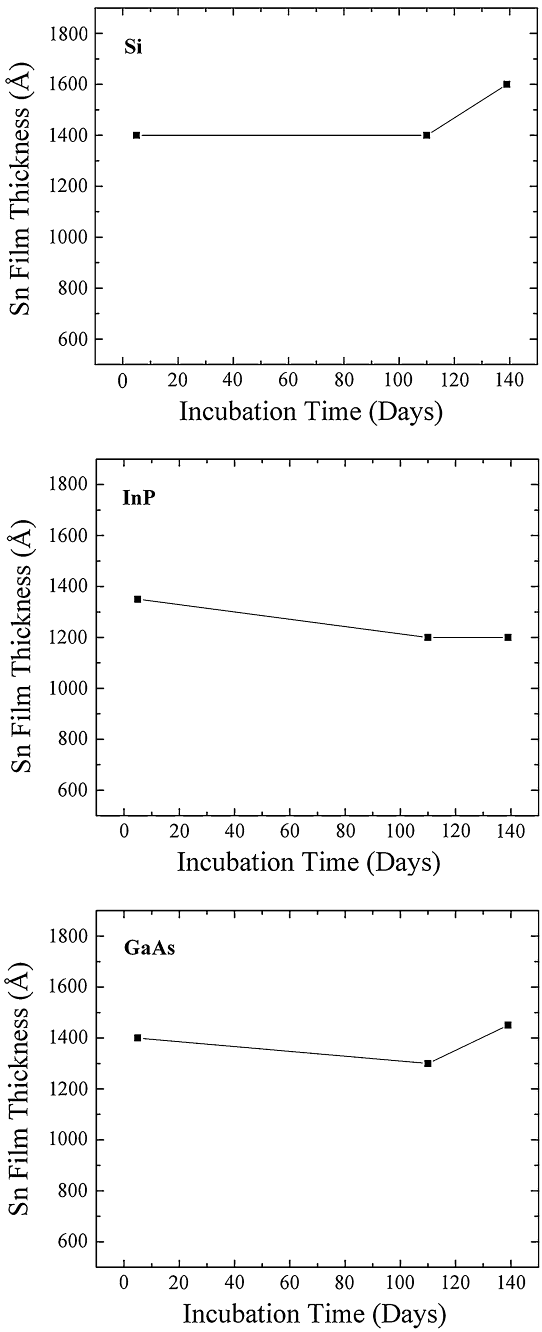


Table 2.17 Whisker growth possibilities for Sn film depletion on GaAs

	Whisker density (cm^{-2})	Average length (μm)
100 Å of Sn depletion on GaAs corresponds to…	5,000	28.29
	10,000	14.15
	15,000	9.43
	20,000	**7.07**
	27,378	5.17
	30,000	4.72
	40,000	3.54

The numbers in bold highlight the actual whisker density and average whisker length measured in our SEM for the Sn on GaAs sample (showing that the back of the hand mass conservation calculations along with the Sn depletion observed by RBS, isn't far off from the actually numbers we manually counted in the SEM)

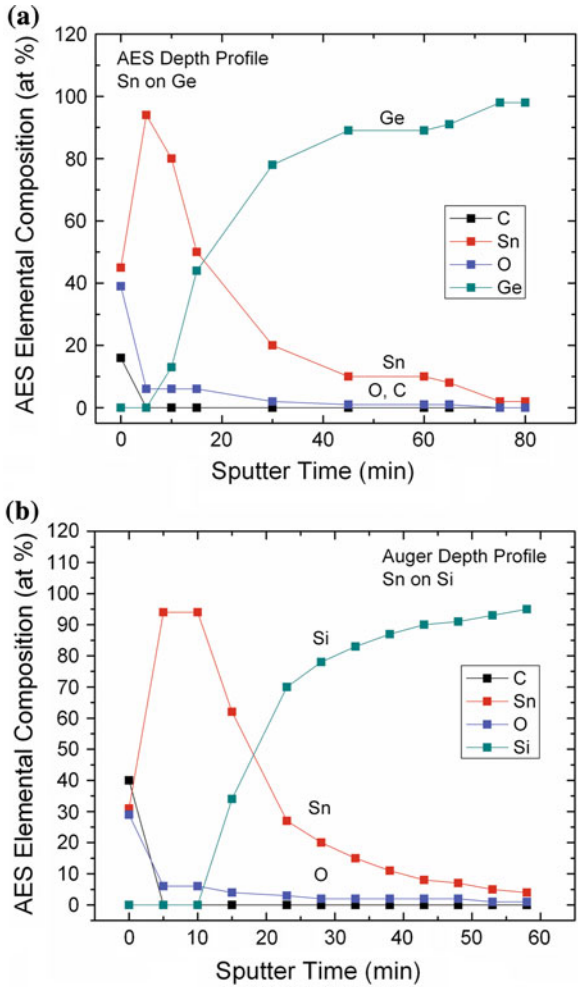


Fig. 2.21 Depth compositions of **a** Sn on Ge, and **b** Sn on Si from the film surface to the substrate as measured by Auger depth profiling. The Ar^+ sputter rate used during profiling was measured to be ~27 Å/min on a standard thin film of SiO_2, commonly used for sputter rate determinations in AES

39,167 whiskers/cm^2 respectively). Glass produced the fewest amount of whiskers (1,703 whiskers/cm^2). InP, InAs, and GaAs have similar, intermediate whisker densities ($\sim$21,000–27,000 whiskers/cm^2). The substrates yield markedly different whisker densities over the first 54 days of incubation but from 54–116 days the *increases* in whisker density are *similar* (glass is a notable exception). The largest whisker producers in this study, Si and Ge, have whisker densities over 22X of 1,500 Å Sn on brass exposed to RT/RH after similar incubation periods. Though the Sn on Ag produced significantly higher whisker numbers than on Si or Ge, it is clear that an IMC is not necessary to produce large numbers of whiskers.

Most of the Sn/semiconductor combinations produced similar average whiskers lengths (6.5–8.3 μm). By comparison to previous cases studied in our laboratory, this length is just slightly shorter than Sn on Ag ($\sim$ 8.5 μm), but much less than Sn on brass exposed to RT/RH (14.2 μm) after similar incubation periods. Sn on glass was an exception, producing an average whisker length of only 2.5 μm.

RBS studies show evidence of the slight Sn film depletion expected during whisker growth, owing to the mass balance that must occur when forming Sn whiskers. We observe a decrease of $\sim$100 Å in the thickness of the deposited Sn film during the incubation period (130 days), which roughly agrees with previous Sn depletion studies of whisker growth from Sn on Ag using AES depth profiling. The fact that identical RBS results were obtained over two widely separated analysis positions on the film surface support the notion of long-range lateral movement of Sn to the whisker shaft during whisker growth. As stated above, direct evidence of such lateral diffusion of Sn during whisker growth was reported in elegant tracer experiments performed by Woodrow [5] and explains why smoother surfaces tend to produce larger whisker numbers, even when IMC formation is absent.

AES depth profiling studies indicated diffusion between the deposited Sn film and semiconductor/insulator substrates during the incubation period at room temperature and humidity conditions. No simple correlation due to CTE mismatches was found between the various semiconductor substrates (having similar CTEs) and Sn whisker growth.

2.5 Whisker Growth Under Different Film Stress Conditions

Most investigators agree that compressive stress in Sn films is the primary driving force behind whisker growth [15], yet little has been reported about the possible, more controversial role of tensile stress [10, 16]. The goal of the work reported here is to produce measurable intrinsically induced thin film stress states (tensile, no stress, and compressive) in Sn and study the effects on whisker growth under the different stress conditions. Our motive for investigating sputter-deposited (rather than electroplated) Sn films is due in part to the relative ease in fabricating films with various stress states in sputtered films (shown below). Further, control of the film stress and prudent selection of film systems which do not grow intermetallic compounds and have minimal CTE mismatches allows for easier elucidation of the fundamental mechanisms impacting whisker growth.

Numerous studies of Sn whiskers have emphasized the role of intermetallic compound formation at the tin-substrate interface, which typically induces a high compressive stress state in the film [10, 17]. To eliminate the complications of intermetallic compound (IMC) formation, all Sn films in this study have been deposited on Si, since the binary phase diagram for Sn-Si shows that Sn-Si IMCs do not form at room temperature. We produce the various stress states through sputter deposition. By controlling the background argon pressure during sputtering, the desired stress state can be dialed into the film [13].

A pure Sn sputter target (99.999 %, Kurt Lesker Co) was used to deposit 2,000 Å Sn films on Si wafer substrates ($\sim 1 \times 1$ cm) in our magnetron sputtering system. The film thickness was verified by stylus profilometry over a step edge in the deposit. The Sn films were sputtered with background argon pressures of 2–3, 8, and 19 mTorr to produce intrinsic compressive stress, no stress, and tensile stress states respectively in the Sn films. After depositing the sputtered Sn films, the samples were incubated under ambient room temperature/humidity (RT/RH) conditions followed by periodic whisker counts for many months using a Cambridge scanning electron microscope (SEM).

In early work on thin film stress, Hoffman and Thornton [13] specified regions of compressive, no stress, and tensile stress states depending on the background Ar gas pressure in the sputter system. For the case of Sn films, compressive stress results when using a background Ar pressure from $\sim$1–6 mTorr and tensile stress is produced with 10–100 mTorr. The “no stress” state has a very narrow (7–9 mTorr) gas pressure range, which creates difficulties in duplicating the “zero” stress state determined in the original Hoffman work due to gauge pressure variations. In our sputter system, the Ar pressure is measured using a Convectron gauge, which measures the heat loss from a sensor wire that is maintained at constant temperature. The heat loss is converted into gas pressure, but it varies with the gas and results in varying gauge sensitivities which can be adjusted in modern gauges. Since the method of pressure measurement in the Hoffman system was not reported, it is not surprising that the critical zero stress pressure may vary slightly between sputter systems depending on the geometry and pressure gauge.

The stress states were examined/verified by curvature measurements using a Veeco Dektak diamond-tipped stylus profilometer. By taking 8 mm line scans across the surface (along perpendicular directions) and measuring the radius of curvature, R, of the specimen, Stoney’s equation can be used to determine the stress in the Sn film. To obtain R, each profilometer scan was fit with a 5th order polynomial by the method of least squares [18] to obtain y(x), the vertical displacement (μm) of the stylus as a function of the lateral displacement (μm). The radius of curvature, R, was then calculated by:

$$R(x) = \frac{(1 + y'^2)^{\frac{3}{2}}}{y''}$$

where $y' = dy/dx$ and $y'' = d^2y/dx^2$, which are then evaluated at x = position of maximum curvature in profilometer scan to obtain a value for R. The radius of curvature was then used to calculate the stress by Stoney's Eq. [18], assuming an initially flat substrate:

$$\sigma = \frac{1}{6R}\frac{E_s}{1 - \upsilon_s}\frac{t_s^2}{t_f}$$

Here σ is the film stress, E_s is Young's modulus (160 GPa), υ_s is the Poisson ratio (0.27) [19], t_s is the substrate thickness (500 μm) and t_f is the film thickness. A more general form of Stoney's equation that accounts for the effect of intermetallic (IMC) growth [20] on curvature is unnecessary for films which do not form IMCs.

After a month (28 days) of incubation at ambient room temperature/humidity conditions, the growth of Sn whiskers on the stressed film specimens was evaluated by SEM. The whisker densities were determined by manually counting whiskers over ten equal representative areas (~275 × 275 μm) on the surface. Table 2.18 shows the whisker growth statistics. Each stress state condition produced whiskers after 28 days of incubation. High whisker densities are observed for both the compressive and tensile states (4,585 and 7,991 whiskers/cm^2 respectively). The observation of whiskering in both tensile and compressive states is in agreement with earlier work in our laboratory with "imposed" external stress states formed by deliberate coupon curvature [21]. There are also whiskers observed for the "zero" stress state, but the density is comparatively low (<1,000 whiskers/cm^2). The tensile stressed film produced the longest average whisker length (16.5 μm) while the compressive (4.3 μm) and "zero" (2.3 μm) stress states created much smaller average whisker lengths.

Table 2.19 shows the whisker statistics after an additional 2 months of incubation (total of 96 days). All samples show increases in whisker density and average whisker length. Films under compression and tension continue to produce

Table 2.18 Whisker statistics after 1 month of incubation for Sn stress states

Sn film state	Whisker density (cm^{-2})	Average whisker length (μm)
Compressive	4,585	4.3
Zero	786	2.3
Tensile	7,991	16.5

Table 2.19 Whisker statistics after 3 months of incubation for Sn stress states

Sn Film state	Whisker density (cm^{-2})	Average whisker length (μm)
Compressive	15,850	5.3
Zero	4,061	3.4
Tensile	12,051	26.8

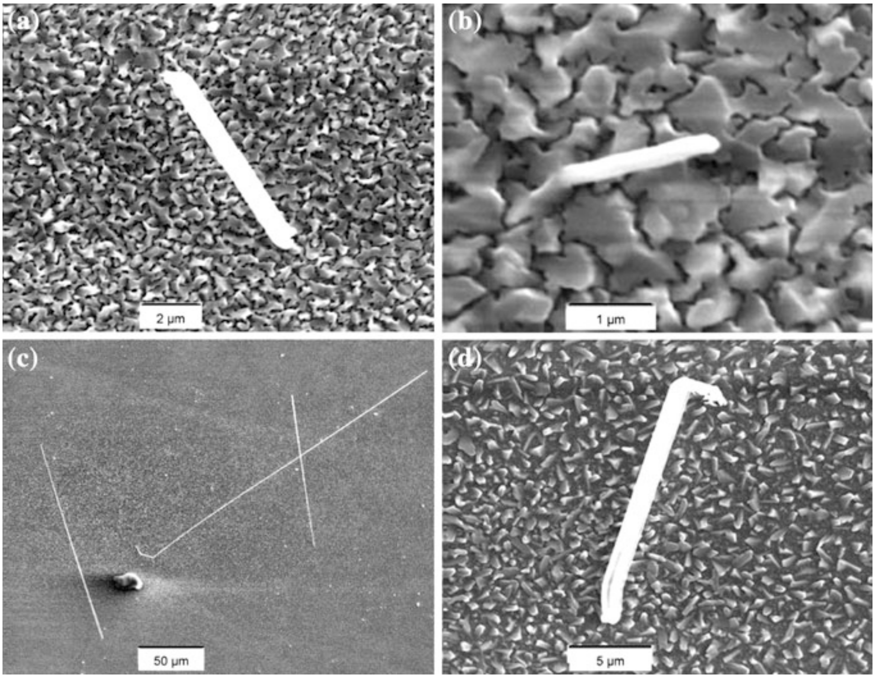


Fig. 2.22 Representative SEM photographs of whiskers produced on Sn films under **a** compressive stress, **b** "zero" stress, and **c**, **d** tensile stress

the highest whisker densities. However, the Sn films under compression are now producing more whiskers than the films under tension. During the additional 2 months of incubation, the zero stress specimen retains the smallest whisker density (1/3 and 1/4 the densities observed in the tensile and compressive stressed films respectively) and the shortest average whisker length (3.4 µm).

Representative high aspect ratio whiskers produced on the various films is shown in Fig. 2.22. The photograph in Fig. 2.22c shows much longer whiskers than in a or b, representing the significant increase in average whisker length observed on films under tension.

Experimental verification of the sputtered film stress states are shown in Fig. 2.23, measured after 3 months of incubation. Negative stress values represent compressive stress (convex surface) and positive values mean tensile stress (concave surface) [18]. The stress values were calculated to be -1.85×10^{11} dyn/cm^2 (compressive); 9.8×10^9 dyn/cm^2 (tensile); and the "unstressed" stress state was 9.83×10^8 dyn/cm^2. The stress values signify the average stress in the film at the 3 month time marker and do not give any indication of the existence of stress gradients in the film, which would require more exhaustive, time-dependent measurements.

The "unstressed" state appears to have no curvature in Fig. 2.23a, but when a higher resolution vertical scale factor is used, there is a *slight* curvature. We believe

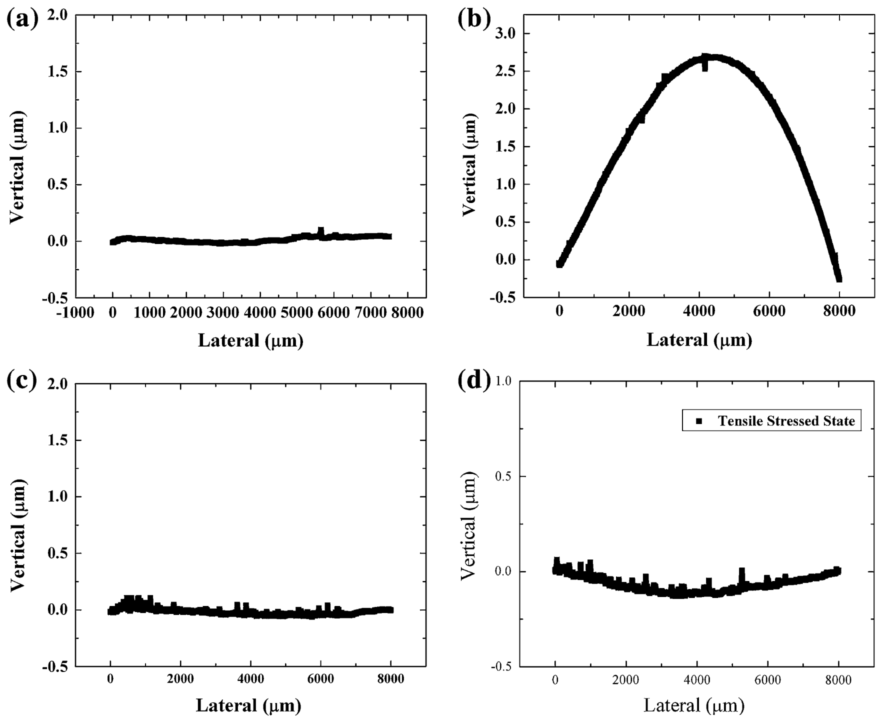


Fig. 2.23 Stylus profilometer topography scans **a** Si substrate only (no sputtered Sn film), **b** Sn film under compression, **c** Sn film with "zero" stress, and **d** Sn film under tension

the "zero" stress value is not precisely zero due to (1) the difficulty when trying to "hit" the narrow argon pressure range needed to attain zero stress; and, (2) pressure gauge variations and slight geometrical differences between Hoffman's magnetron sputtering system and ours; (3) the fact that we are observing whisker production. It is common when measuring stress in Si wafers using profilometry to expect a measurement uncertainty of the order of 1×10^8 dyne/cm^2 [22].

Figure 2.24 illustrates the measured whisker density versus incubation time for each sample. All samples show increasing whisker growth with time, regardless of whether they are producing large or small quantities of whiskers. After ~100 days of incubation, there is no evidence of a plateau in the whisker density versus incubation time graphs.

This work gives evidence of whisker growth from sputter-deposited Sn films under *both* compression and tension. While there are questions about how the film stress evolved over time since deposition, the curvature results give some level of confidence that the initial "dialed" up stress states still existed 3 months later. At that time, the films under compression had produced ~15,000 whiskers/cm^2 and

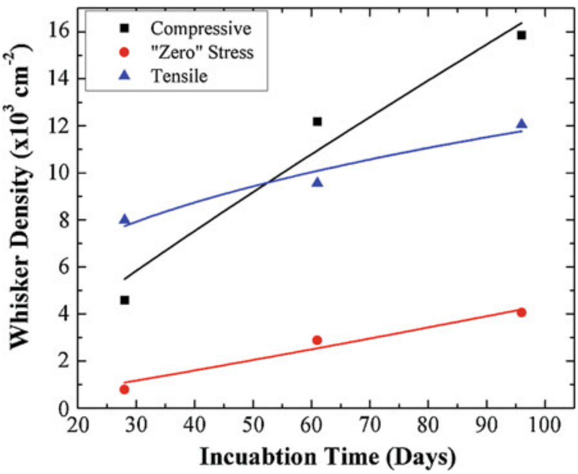


Fig. 2.24 Plot of whisker density versus incubation time for Sn film stress states exposed to RT/RH conditions

the films under tension had produced ~12,000 whiskers/cm^2. In contrast, the "unstressed" film had generated ~4,000 whiskers/cm^2 after 3 months. The lower whisker numbers on the unstressed film is better understood after verifying that the *actual* stress in the "unstressed" Sn film had a comparatively low, but nonzero, (tensile) value of 9.83×10^8 dyn/cm^2. In contrast, the compressive and tensile stress values were an order of magnitude higher than the "unstressed" film.

While films under compression produced the largest whisker densities after 3 months, the films under tension grew the longest whiskers (average whisker length of ~27 μm) compared to the film under compression (~5 μm). The "zero" stress film had an average whisker length of only ~3.5 μm. The longest whisker was produced under tension and reached 338 μm! The stress values calculated using Stoney's equation were in the expected range for Si substrates and in accordance with the desired compressive film state (negative stress value) and tensile film state (positive stress value).

Although rare, the literature shows that whiskers can be produced under tensile stress. Xu et al. [16] observed whisker production in electroplated Sn films on Cu, aged at 50 °C for up to 10 months. The specimens were subjected to externally imposed compressive and tensile stress. The tensile specimens started producing whiskers after 4 months and, after 10 months; there were more than 45,000 whiskers. The films under compression produced greater whisker numbers than films under tension, although no actual stress values were reported in that work. Studies in our laboratory [21] using sputtered Sn on brass under imposed tension and compression also showed whiskers under both stress states. The whisker densities under each condition of stress increased as the magnitude of the tensile and compressive forces increased.

2.6 Whiskering from Sn Alloy Films

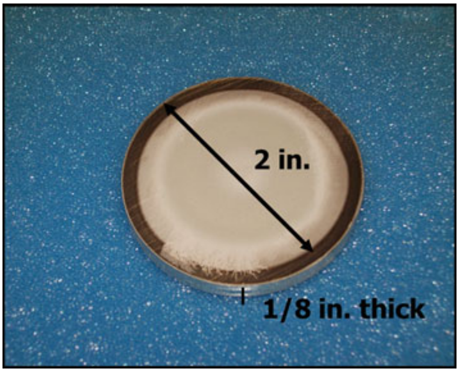
Since the Pb-free movement mandated the removal of Pb entirely from the electronics supply chain, there has been an emergence of SAC solder alloys. The question is whether SAC alloys having high mole fractions of Sn are whisker-prone. The answer is yes. Handwerker et al. [23] from Purdue University found whisker growth on electroplated SAC405 soldered surfaces. The whiskers were observed on the leads of a MOSFET device, both after life testing (20 days at 65 °C/25 %RH with a 40 CFM blower) and under normal storage conditions. Whiskers have also been observed [24] on hot dipped SAC305 surface mount resistor terminations after 500 h at 85C/85 %RH plus 500 temperature cycles from −55 to 125 °C, and from SnCu [25] and SnAg [26] electrodeposits.

In fact, even eutectic Sn-37Pb alloys can produce whisker growth under the right stress conditions. Chason et al. [27] observed whiskering from electrodeposited Sn-10 %Pb alloy films on multilayer samples fabricated on Si substrates. The layer structure was created by electron beam deposition with a 15 nm Ti adhesion layer followed by 600 nm Cu and a 1200 nm Sn alloy film. NASA and the QSS Group [28] has observed SnPb alloy whiskers which have created electrical shunts. In a 2003 evaluation of GaAs laser diode arrays at NASA Goddard Space Flight Center, whiskers were observed emanating from reflowed eutectic Sn-37Pb solder die attach material. The maximum whisker lengths ranged from 25 to 30 μm while the shunting distance (heat sink to laser diode) was only 2.5–3.0 μm. Whiskering within 30 min has been witnessed from a coating layer of Sn60/Pb40 hot air solder leveling under compressive stress conditions [29]. Thick electroplated films of 3, 7, and 16 μm have shown no whiskering from the incorporation of only 2 %Pb (Sn98/Pb2) after a month of incubation [20]. Electrodeposited films of 10 μm (>83X thicker than our 1,200 Å film, described below) produced no whiskering after 6 months with the incorporation of only 5 %Pb in the Sn film [30].

In our experiments involving whiskering on alloyed materials, we were asked by a CAVE3 client to determine if *sputtered* films of SAC305 and Sn-37Pb were whisker prone. This posed a challenge, as sputter targets of these materials do not exist, so we had to make our own targets. The solution was to make a round glass mold with dimensions matching our sputter target size (2 in dia. × 1/8 in thick). Bulk specimens of SAC 305 and Sn-37Pb were then melted and poured into the glass mold, followed by water quenching. The glass mold was then broken, the target was removed, and then sanded down for a smooth distinct shape compatible with our sputter system. The custom sputter target is shown in Fig. 2.25.

SAC305 and Sn-37Pb thin films were subsequently sputter-deposited under compressive stress conditions onto electrochemically polished brass (Cu63/Zn37). The resulting film thicknesses were ~2,400 Å (SAC305) and ~750 and ~1,200 Å (Sn-37Pb), measured by RBS. When doing sputter deposition of alloy

Fig. 2.25 Custom made sputter target



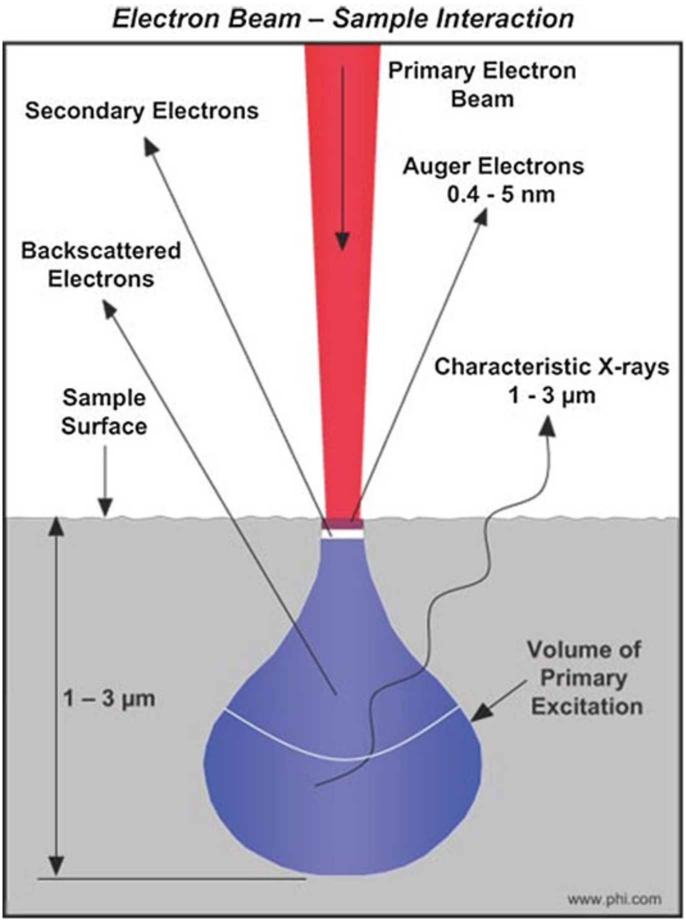


Fig. 2.26 The signal categories emanating from a surface during electron beam excitation. The signal from EDX typically originates from 1 to 3 microns below the surface (http://www.phi.com/surface-analysis-techniques/aes.html)

Table 2.20 EDX element composition sputtered (a) SAC, and (b) SnPb Films

Element	Weight	Atomic
a		
Cu	0.16	0.29
Ag	3.02	3.30
Sn	96.83	96.40
b		
Sn	67.04	78.02
Pb	32.96	21.98

films, the issue of congruency arises. Congruency means that the deposited film contains the same ratio of elements as the sputter target. Incongruent sputtering, by contrast, occurs when one element (e.g., Sn) is sputtered preferentially, which results in a film composition which differs from the target composition. To verify congruency, it is necessary to determine the mole fraction of elements in the sputtered film. For this purpose we used energy dispersive X-ray spectroscopy (EDX), under two precautions. First, since the SAC was deposited on brass, the EDX Cu peak is a superposition of Cu in SAC305 and Cu in the brass substrate. This forced the test to be done with SAC305 deposited on a silicon wafer instead of brass. Second, there is a problem when doing EDX on thin films having to do with the signal sampling volume. Specifically, EDX is more properly a volume materials technique, not a surface analysis technique. The difference is important when analyzing thin films. Shown in Fig. 2.26, the X-ray signals generated during a standard EDX analysis originate from a pear-shaped volume ~1–3 μm under the surface, which is problematic when doing analyses on submicron thin films. The EDX data obtained from a submicron film is dominated by the signal from the substrate signal and not from the desired thin film. It was therefore necessary to deposit thicker layers than typical and to utilize glancing-angle EDX to maximize the fraction ($\cos\theta$ dependence) of X-ray signal from the film. The conclusion (Table 2.20) from EDX was that both SAC305 and Sn-37Pb had been sputter deposited congruently.

After sputter deposition, the SAC 305 and Sn-37Pb films were incubated under ambient RT/RH. Whisker statistics recorded after a month of incubation are shown in Table 2.21. At this time, the thinnest, 750 Å Sn-37Pb alloy film was producing

Table 2.21 Whisker statistics for Sn alloy films after 36 days of incubation

Film	Thickness (Å)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
SAC 305	2400	1,048	2.3	0.7	2
SnPb	750	3,537	2.2	0.4	2
	1200	0	NA	NA	NA

Table 2.22 Whisker statistics for Sn alloy films after 190 days of incubation

Film	Thickness (Å)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
SAC 305	2400	33,665	4.6	5.8	2
SnPb	750	4,454	3.9	1.9	2
	1200	0	NA	NA	NA

Table 2.23 Whisker statistics for Sn alloy films after over a year of incubation

Film	Thickness (Å)	Whisker density (cm^{-2})	Average whisker length (μm)	Standard deviation (μm)	Mode
SAC 305 (590 days)	2,400	147,498	5.0	5.3	2
SnPb (407 days)	750	7,991	3.4	2.0	2
	1,200	524	2.3	0.5	2

the greatest number of whiskers (~3,500 whiskers/cm^2) while the 1,200 Å Sn-37Pb film produced no whiskers. The SAC film grew ~1,050 whiskers/cm^2 over a one month period with an average whisker length ~2 μm. After 190 days of incubation (Table 2.22), the rate of SAC whisker production has increased greatly (>33,600 whiskers/cm^2). In contrast, the thinner Sn-37Pb film has only slightly increased whisker growth while the thicker Sn-37Pb film is still void of any whiskers. The average whisker lengths are low on both films, with SAC 305 producing the greatest average whisker length of 4.6 μm.

Table 2.23 shows whisker statistics after a year of incubation. We finally see whisker growth (albeit, near-zero) from the 1,200 Å Sn-37Pb film (524 whiskers/cm^2), corresponding to only 5 whiskers for every square millimeter of surface. The thicker 750 Å Sn-37Pb film has modest whisker numbers after one year, while SAC has produced >147,000 whiskers/cm^2. The data highlights the ability of incorporated Pb to suppress whiskers and shows that, under specific stress conditions, both Sn-37Pb and SAC305 will form whiskers. Figures 2.27 and 2.28 show representative whisker morphologies from SAC and SnPb films respectively.

The whisker density versus incubation time for sputtered SAC305 and Sn-37Pb films are compared in Fig. 2.29. It is clear that the SAC film is producing much larger whisker numbers than the SnPb films. The thinner, 750 Å, SnPb film is producing some whiskering in time, but the 1,200 Å SnPb film is barely producing any whisker growth (even after a year of incubation).

In conclusion, it is apparent that whisker growth can occur on Sn alloyed deposits such as SAC. After 407 days of incubation in ambient RT/RH, we find

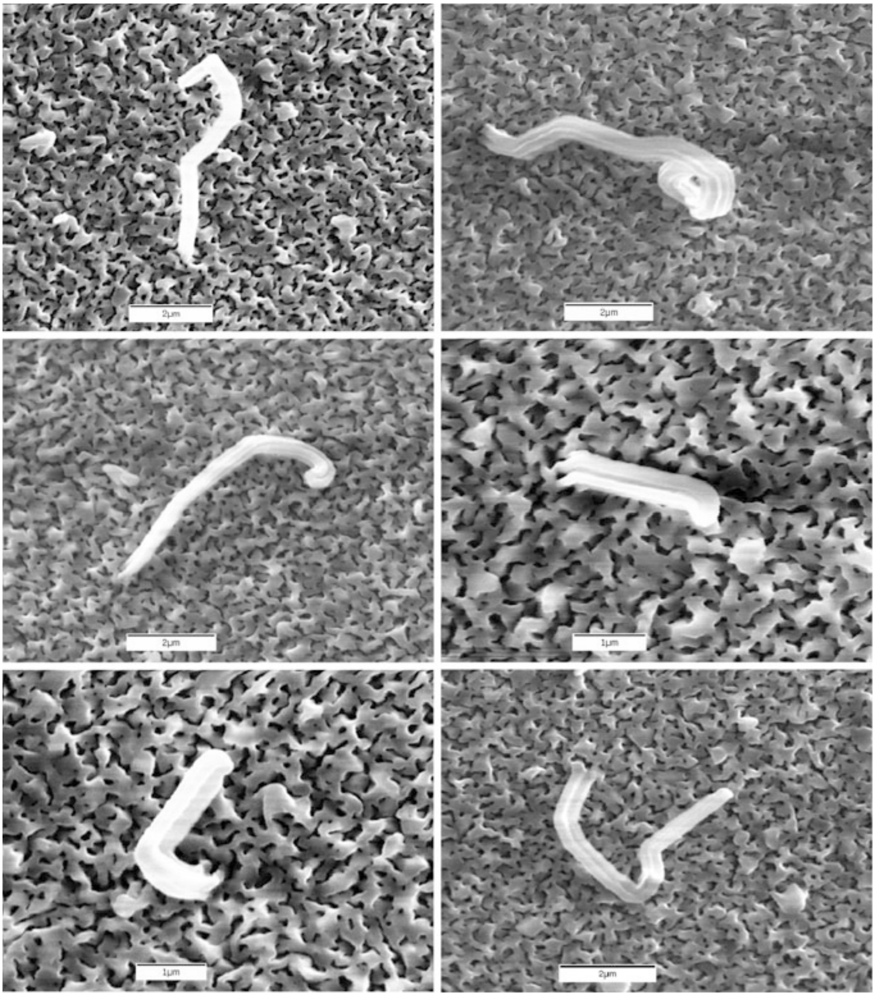


Fig. 2.27 SEM images of whiskers growing from SAC 305 film

over 7,900 whiskers/cm^2 on the 750 Å Sn-37Pb specimen. Comparing this to 750 Å of pure Sn on brass after similar incubation periods, the Sn film produced $\sim$1.75X the whisker density of the Sn-37Pb film, with $>$ 5X the average whisker length. This is not surprising, since the corporation of Pb in Sn is known to

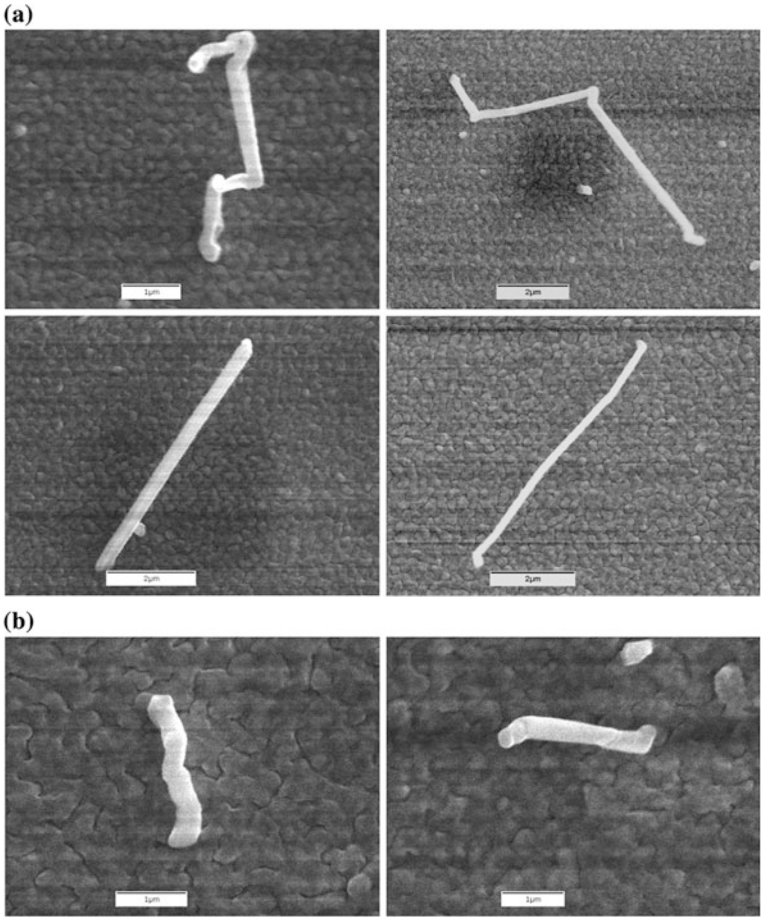


Fig. 2.28 SEM images of whiskers growing from SnPb films **a** 750 Å, and **b** 1,200 Å

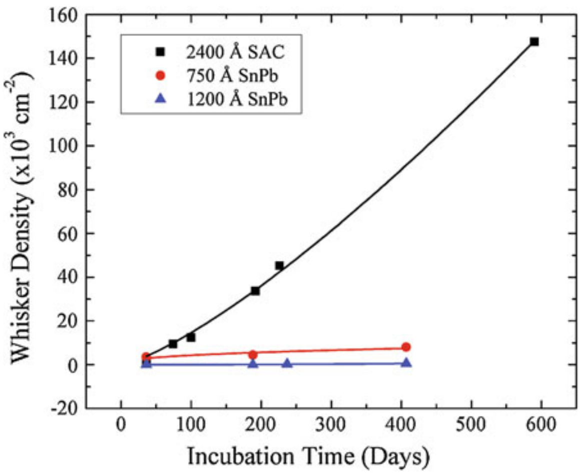


Fig. 2.29 Whisker density versus time plot for Sn alloy films

mitigate whisker growth. In fact, Chason et al. [27] observed whiskering from electrodeposited Sn-10 %Pb alloy films and found that the stress developed in the SnPb film was much less than that in the pure Sn films. This is in agreement with the whisker statistics above.

References

1. P. Oberndorff, M. Dittes, L. Petit, C.C. Chen, J. Klerk, E.E. de Kluizenaar, *Tin Whiskers on Lead-free Platings*. Semiconductor Technology Symposium, Advanced packaging Technology, vol. 2 (2002), pp. 51–55
2. P. Oberndorff, M. Dittes, P. Crema, Whisker Testing: Reality or Fiction? in *Proceedings of the IPC/Soldertec 2nd International Conference on Lead Free Electronics*, Amsterdam (2004) CD-ROM
3. Purchased from Goodfellow Cambridge Limited, Ermine Business Park, Huntingdon, PE29 6WR, Units C1 & C2, England
4. J.A. Thornton, D.W. Hoffman, Internal stresses in Titanium, Nickel, Molybdenum, and Tantalum films deposited by cylindrical magnetron sputtering. J. Vac. Sci. Technol. **14**(1), 166 (1977)
5. T.A. Woodrow, Tracer diffusion in whisker-prone tin platings, in *Proceeding of STMA International Conference*, Rosemont, IL, 24-28 September 2006
6. M.J. Bozack, E.R. Crandall, C.L. Rodekohr, R.N. Dean, G.T. Flowers, J.C. Suhling, High lateral resolution auger electron spectroscopic (AES) measurements on high-aspect ratio Sn whiskers on brass. IEEE Trans. Electron. Packag. Manuf. **33**(3), 198–204 (2010)
7. Purchased from Ted Pella, Inc., PO Box 492477, Redding, CA 96049-2477
8. Purchased from Electron Microscopy Sciences, 1560 Industry Rd., Box 550 Hatfield, PA 19440
9. C. Xu, Y. Zhang, C. Fan, J. Abys, Understanding whisker phenomenon, Part II, competitive mechanisms, in *Proceedings of the APEX Meeting*, San Diego (2002)
10. Y. Zhang, C. Fan, C. Xu, O. Khaselev, J.A. Abys, Tin whisker growth: substrate effect understanding CTE mismatch and IMC formation. CircuiTree **7**, 70–82 (2004)

11. Semiconductors on NSM, http://www.ioffe.ru/SVA/NSM/Semicond/index.html
12. The Engineering ToolBox, http://www.engineeringtoolbox.com/linear-expansion-coefficients-d_95.html
13. J.A. Thornton, D.W. Hoffman, Stress-related effects in thin films. Thin Solid Films **171**, 5 (1989)
14. C.L. Rodekohr, M J. Bozack, G.T. Flowers, J.C. Suhling, Influence of substrate surface roughness on sn whisker growth, in *Proceedings of the 54th IEEE Holm Conference on Electrical Contacts*, October 2008, p 245
15. G.T. Galyon, C. Xu, S. Lal, B. Notohardjono, A. Frye, ECTC2005 iNEMI Tin Whisker Modeling Committee, iNEMI Tin Whisker Workshop, *in IEEE Electronics Components Technology Conference*, Lake Buena Vista, FL 2005
16. C. Xu, Y. Zhang, C. Fan, J.A. Abys, Understanding whisker phenomenon, the driving force for whisker formation. Circuitree 94–104 (2002)
17. B.Z. Lee, D.N. Lee, Spontaneous growth mechanism of tin whiskers. Acta Metall. **46**(10), 3701–3714 (1998)
18. M. Zecchino, T. Cunningham, *Thin Film Stress Measurement Using Dektak Stylus Profilers*. (Veeco Instruments Inc., 2004)
19. T. Chudoba, N. Schwarzer, F. Richter, Determination of elastic properties of thin films by indentation measurements with a spherical indenter. Surf. Coat. Technol. **127**, 9 (2000)
20. W.J. Boettinger, C.E. Johnson, L.A. Bendersky, K.W. Moon, M.E. Williams, G.R. Stafford, Whisker and Hillock formation on Sn, Sn-Cu and Sn-Pb electrodeposits. Acta Mater. **53**, 5033–5050 (2005)
21. C.L. Rodekohr, G.T. Flowers, M.J. Bozack, R.N. Dean, R.L. Jackson, P. Lall, Influence of quantifiable extrinsic stresses on tin whisker growth, in *Proceedings of the ASME International Design Engineering Technical Conferences and Computers and Information in Engineering Conference*, IDETC/CIE, San Diego 2009
22. M.E. Thomas, M.P. Hartnett, J.E. McKay, The use of surface profilometers for the measurement of wafer curvature. J. Vac. Sci. Technol., A **6**, 2570 (1988)
23. C.A. Handwerker, Tin whisker and surface defect formation of electrolplated films and reflowed joints, in *CALCE Symposium on Part Reprocessing, Tin Whisker Mitigation, and Assembly Rework/Repair* 2008
24. P. Bush, SUNY Buffalo from J. Brusse/Perot Syst, Some Examples of “Whiskers” from Tin-Based Alloys (2009), http://www.hlinstruments.com/RoHS_articles/Tin%20whiskers%20from%20tin%20alloy%20coatings.pdf
25. SWATCH Petition to EU TAC for RoHS Exemption (2006)
26. N. Asrar, O. Vancauwenberghe, S. Prangere, Whiskers from SnAg eutectic solder, tin whiskers formation on an electronic product: a case study. ASM Int (2007)
27. E. Chason, N. Jadhav, W. L. Chan, L Reinbold, and K. S. Kumar, Whisker formation in Sn and Pb-Sn Coatings: role of intermetallic growth, stress evolution, and plastic deformation processes. Appl. Phys. Lett. **92**, 171901 (2008)
28. H. Leidecker, C. Greenwell, J. Brusse, *Whiskers of Tin-Lead (Sn-Pb) on REFLOWED Die Attach Solder Used in the Manufacture of a Laser Diode Array*. (NASA Goddard Space Flight Center and QSS Group, Inc., 2003), http://nepp.nasa.gov/whisker
29. J. Liang, N. Dariavach, D. Shangguan, Tin whisker nucleation and growth on Sn-Pb eutectic coating layer inside plated through holes with press-fit pins. IEEE Comp. Pack. Tech. **31**, 1 (2008)
30. W. Zhangz, F. Schwager, Effects of lead on tin whisker elimination efforts toward lead-free and whisker-free electrodeposition of tin. J. Electrochem. Soc. **153**, 5 (2006)

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