

Crystallographic Texture and Whisker Growth in Electroplated Sn and Sn-Alloy Films

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Abstract

Tin whisker growth poses a continued reliability concern for Pb-free electronic systems. The fundamental mechanisms behind the spontaneous growth of these metallic filaments are not well understood and a greater understanding is required to develop mitigation strategies. Published data shows that variations of plating process parameters can produce electroplated films with clearly different crystallographic textures, and for electroplated Sn and Sn-alloy films changes in crystallographic texture may lead to different rates of whisker growth.

In this work, the relationship between materials, processing parameters, crystallographic texture, and whisker propensity is examined. Four electrolyte compositions were used to electroplate Sn and Sn alloy films with different compositions and microstructures on phosphor bronze and pure Cu substrates. Pole figures and inverse pole figures created using x-ray diffraction were used to determine the quantitative crystallographic texture of films as a function of processing parameters such as current density. The tendency for these films to form whiskers or other surface defects was categorized by surface defect density and type. The relationship between film texture, film composition, and whisker formation is presented. These data suggest that while the optimal crystallographic texture is not yet known, it may be possible to use x-ray texture data as a guideline for controlling and monitoring plating processes to reduce the tendency of films to form whiskers.

Introduction

The spontaneous growth of Sn whiskers in electronic systems has been recognized as a serious electrical reliability risk since being discovered in 1951[1]. Despite the age of the problem, the mechanisms behind whisker growth are not well understood. A compressive stress gradient that leads to a whisker forming from one grain out of 1000-10,000 grains is believed to be the driving force behind whisker growth [2]. The source of this stress gradient can be related to a number of variables including but not limited to plating stresses [2] or the formation of the Cu_6Sn_5 intermetallic at the interface between the plating and the copper substrate [3]. Co-depositing Cu with Sn has also been found to increase the magnitude of the as-plated and steady state compressive stress and the propensity to whisker by several proposed effects, including hindering grain boundary motion [4][5].

Shortly after the discovery of tin whiskers, S.M. Arnold published recommendations to minimize whisker growth [6]. According to Arnold, the “best results” were from co-depositing Pb with Sn. This became the industry standard, but Pb-free processing requirements have created a need for new solutions.

In the work by Arnold, other conditions were found to influence the propensity of a film to whisker. Two of these conditions included the current density during deposition and the composition of the electrolyte, factors that are known generally to influence the crystallographic texture of electrodeposited films [7].

In this work, the quantitative crystallographic texture of Sn-based electrodeposited films was calculated using x-ray diffraction (XRD) with GADDS and the Rietveld refinement program MAUD. Using the same base electrolyte containing commercial brighteners and levelers for deposition, the effects of current density, substrate type, and Cu and Pb co-deposition on texture and propensity to whisker were evaluated.

Crystallographic Texture and Whisker Formation

The significance of texture for the growth of Sn whiskers was outlined by Lee and Lee [8]. They calculated that the expected strain for a given stress could vary by more than 300% depending on the crystallographic orientation due to the anisotropic elastic behavior of Sn. For a polycrystalline Sn film under plane stress conditions, elastic anisotropy

would then lead to adjacent grains with different crystallographic orientations and therefore with different out-of-plane strains, depending on the grain boundary conditions. According to Lee and Lee, such differences in crystallographic orientations and out-of-plane strains for adjacent grains could lead to a single grain growing out from its surrounding grains and potentially continuing to grow into a whisker.

The preferred orientations of electrodeposited Sn films using x-ray diffraction (XRD) have been reported in several papers. Using a method comparing the intensity of peaks for a film to a randomly oriented sample, Lee and Lee reported a (100) preferred orientation for films deposited with a current density of 5mA/cm² and (110) for films deposited at 35mA/cm² [8]. Using a similar method Moon *et al.* reported that the substrate could influence the film texture resulting in a (103) preferred orientation for one substrate versus a (101) for another [9]. Recently, Sobiech *et al.* reported a (321) preferred orientation and Frye *et al.* reported preferred orientations for a variety of films including (101), (321), and (001) [10][11]. All of the previously mentioned preferred orientations are measurable using standard XRD techniques except for the (001) [12]. The (001) was determined using pole figures of measurable orientations. These methods do give information regarding preferred orientations but the peak intensity comparison method can only give information regarding the specific peaks measured. Pole figure analysis can only give information on the poles analyzed.

To quantitatively determine the crystallographic texture, it is necessary to evaluate all possible orientation and XRD based methods are capable of doing this. The Rietveld refinement method allows for the deconvolution of complex x-ray spectra [13]. The method has been used for a variety of applications including quantitatively measuring the texture of thin films [14]. Software such as "Materials Analysis Using Diffraction", or "MAUD", has been developed to assist in the quantitative determination of texture [15]. This type of analysis requires multiple diffraction measurements at various sample tilts to gather orientation information with respect to sample coordinates.

A general area diffraction detection system, or GADDS, can be used to decrease the amount of time needed to gather the data necessary for quantitative texture analysis. The detector gathers arcs from the Debye rings instead of just single spots as with standard x-ray diffractometers [16]. This allows for a range of sample tilts (χ) and diffraction angles (θ) to be gathered in one static measurement. An example of the x-ray spectra gathered using

GADDS is shown in Figure 1. This system coupled with MAUD has been used previously to determine the texture of tetragonal lead zirconate titanate [17].

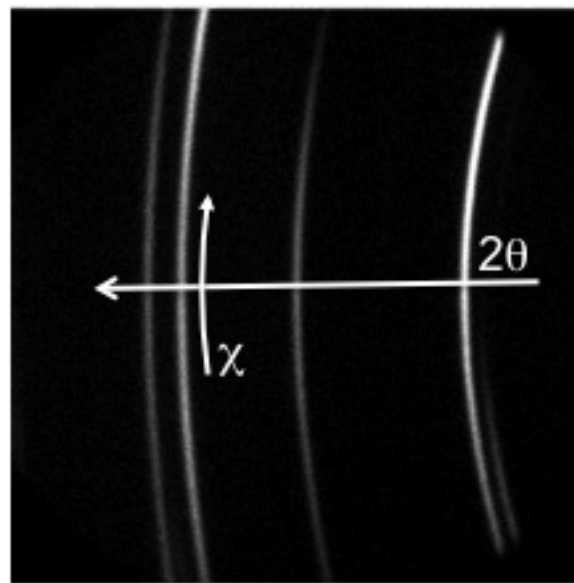


Figure 1: Sample XRD measurements using GADDS collecting a range of 2θ and tilt (χ) angles in a single measurement.

Procedure

Four methanesulfonic acid (MSA) based electrolyte compositions were evaluated: one pure Sn, two different Sn/Cu, and one Sn/Cu/Pb ternary composition. One liter of each electrolyte was prepared with a Sn concentration of 380mmol/L. The two Sn/Cu electrolytes also contained either 1.9 or 7.5mmol/L Cu. The Sn/Pb/Cu contained 1.9mmol/L Cu and 3.6mmol/L Pb. All electrolytes also contained a commercial brightener and leveler.

Pure Cu and phosphor bronze were used as substrate materials. The pure Cu substrates were 1.27mm thick sheets of alloy 101 (ASTM B152), 99.99% pure. The phosphor bronze (ASTM B103) substrates were spring tempered 1.27mm thick sheets. All sheets were machined into 15x15mm coupons for plating. The Cu substrates were electropolished to a scratch-free finish; the phosphor bronze sheets were received scratch free and were not electropolished.

A laboratory rotating cathode apparatus was used for all electroplating. Substrates were attached to the rotating cathode using plater's tape with a 10x10mm area exposed for plating. Tin sheet (99.999% pure) with an exposed area of 15x15mm was used as the static anode. Substrates were plated individually. Each substrate was submerged in 1L of electrolyte in a glass beaker. The samples were then plated with a current density of 20, 60, or

120mA/cm² while rotating. Samples plated at 20 and 60mA/cm² were rotated at the rate of 100rpm during plating. Samples plated at 120mA/cm² were rotated at 200rpm due to excessive hydrogen evolution. Plating time varied as a function of current density. The final thickness of the plating was determined by measuring the change in mass of the coupon. Thicknesses ranged from 8 to 12µm.

Steel substrates were also electroplated for compositional analysis. Substrates were plated in several Cu containing electrolytes with concentrations ranging from 0 to 17mmol/L and a Pb concentration ranging from 0 to 10mmol/L. The composition of the resulting films was analyzed using x-ray fluorescence and was found to vary linearly over the range evaluated[18]. A summary of all films deposited is shown in Table 1.

X-ray reflectance measurements were made using a Bruker AXS diffractometer with a general area detector diffraction system (GADDS) and copper K α radiation with a spot diameter of 0.5mm. Four measurements were made per sample with the detector centered at either 55.332° or 79.472° 2 θ and a tilt angle of either 0° or 35.26°. This allowed for the measurement of all expected peaks between 43° and

90° 2 θ and tilt angles from 0° to 50°. The resulting data were integrated with respect to χ in 5° increments and steps of 0.04° 2 θ .

The resulting crystallographic data were analyzed using the Rietveld refinement software MAUD (Version 2.14). The E-WIMV texture model was applied to the data assuming fiber symmetry and an orientation distribution function resolution of 2.5°. The software was also used to create pole figures and inverse pole figures. Inverse pole figures were independently labeled using an equal area projection and a c/a ratio of 0.546. An inverse pole figure with labeled poles is shown in Figure 2.

Films plated at 60mA/cm² were examined using SEM approximately 150 days after plating. Samples plated at 20 and 120mA/cm² were evaluated 60 days after plating. Sixteen 0.0476 mm² areas were evaluated near the center of the deposited area. The number of defects per area and the type of defect (whisker or hillock) were manually counted. Defect density (#/mm²) was determined by normalizing the number of defects measured in each individual micrograph. The minimum and maximum defect density represents the values for individual micrographs.

Table 1: Composition and plating parameters of electroplated films including preferred orientation (P.O.), angle between the film normal (N) and the c-axis, and defect density. Note: Defect densities were not all measured over the same time period.

Film	Substrate	Current Density [mA/cm ²]	P.O./MRD	Angle b/w N and c-axis	Type	Days after Plating	Defect Density, [# /mm ²]		
							Average	min	max
Pure Sn	Copper	20	(501)/15	70	H	60	12	0	65
Pure Sn	Copper	60	(111)/12	38	H	150	12	0	43
Pure Sn	Copper	120	(001)/105	0	H	60	27	0	65
Sn, 0.1%Cu	Copper	20	(545)/9	35	H,W	60	204	87	326
Sn, 0.1%Cu	Copper	60	(445)/9	32	H	150	333	196	522
Sn, 0.1%Cu	Copper	120	(445)/13	32	H,W	60	60	0	152
Sn, 0.7%Cu	Copper	20	(767)/7	36	H,W	60	270	152	391
Sn, 0.7%Cu	Copper	60	(334)/8	30	H,W	150	327	196	522
Sn, 0.7%Cu	Copper	120	(335)/17	25	H,W	60	388	261	565
Sn, 0.1%Cu, 1.3%Pb	Copper	20	(611)/6	73	--	60	0	0	0
Sn, 0.1%Cu, 1.3%Pb	Copper	60	(001)/30	0	H	150	86	22	239
Sn, 0.1%Cu, 1.3%Pb	Copper	120	(001)/48	0	H,W	60	477	239	782
Pure Sn	Bronze	60	(334)/8	30	H	150	19	0	65
Sn, 0.1%Cu	Bronze	60	(334)/8	30	H	150	10	0	43
Sn, 0.7%Cu	Bronze	60	(335)/8	25	H	150	29	0	152
Sn, 0.1%Cu, 1.3%Pb	Bronze	60	(001)/33	0	H	150	94	22	304

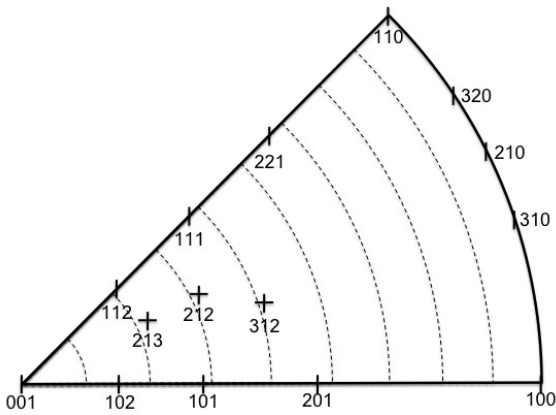


Figure 2: Equal area inverse pole figure for tin with selected labeled poles. Dashed lines represent 10° increments off the 001 pole.

Results

Crystallographic Texture

Inverse pole figures created for all films deposited on bronze are shown in Figure 3; films deposited on Cu are shown in Figure 4. All figures are plotted on a multiples of random distribution (MRD) scale of 0 to 15, are equal area projections, and are with respect to the sample normal. The goodness of fit variable, R_w varied from 18 to 25%. The preferred orientation and MRD are displayed in Table 1.

Differences in crystallographic texture were observed for all three variables; current density, electrolyte chemistry, and substrate material. Increasing current density resulted in a trend toward higher MRD's and a decreasing angle between the c-axis and film normal. Examples of the observed decrease in angle between the film normal and c-axis are shown for both pure Sn and Sn,Cu,Pb films deposited on Cu. For pure Sn, increasing current density leads to a change from a (501) preferred orientation to a (111), to a (001). This corresponds to the c-axis being 70° off the film normal, to 38°, to being aligned with the film normal. The Sn,Cu,Pb films had a preferred orientation of (611) at 20mA/cm² corresponding to the c-axis being 73° off the film normal. Increasing the current density to 60mA/cm² resulted in (001) texture, aligning the film normal with the c-axis. Increasing the current density to 120mA/cm² did not change the preferred orientation but did increase the MRD from 30 to 48 for the Sn/Cu/Pb film.

Co-depositing Cu also influenced the texture. All preferred orientations for the Pb-free Cu containing films on Cu had the c-axis between 25° and 36° off the film normal, regardless of current density. Increasing current density still resulted in a trend of decreasing the angle between the c-axis and the film normal and increasing MRD, but these changes were not as drastic as for the pure Sn films.

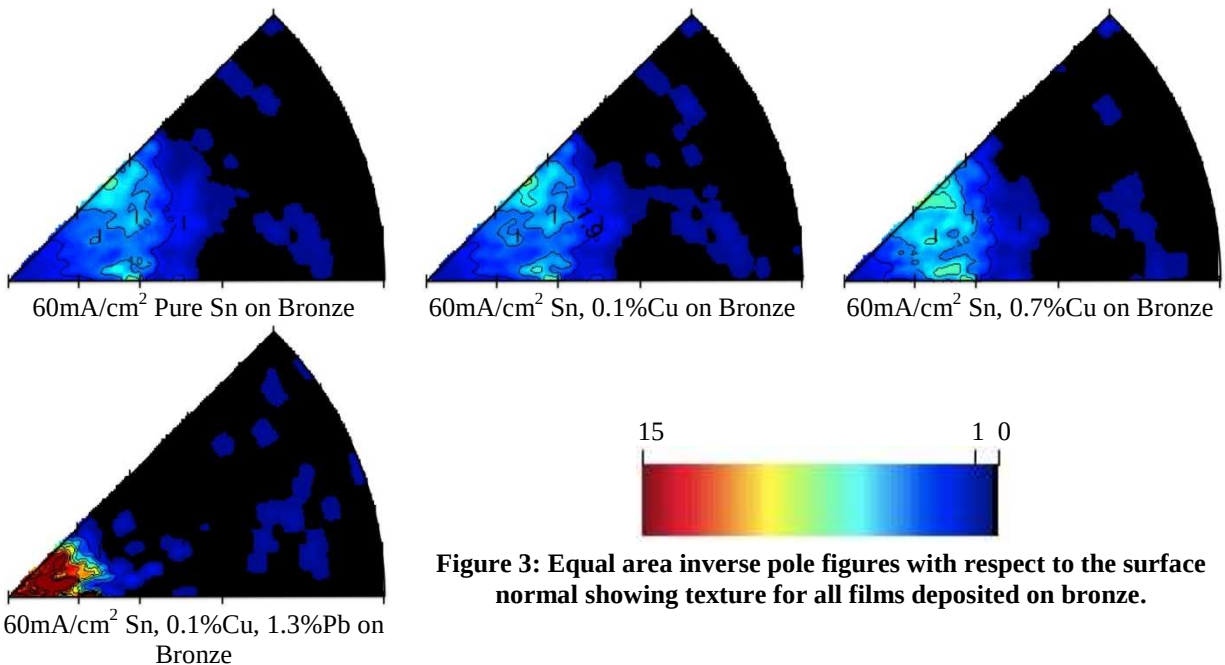


Figure 3: Equal area inverse pole figures with respect to the surface normal showing texture for all films deposited on bronze.

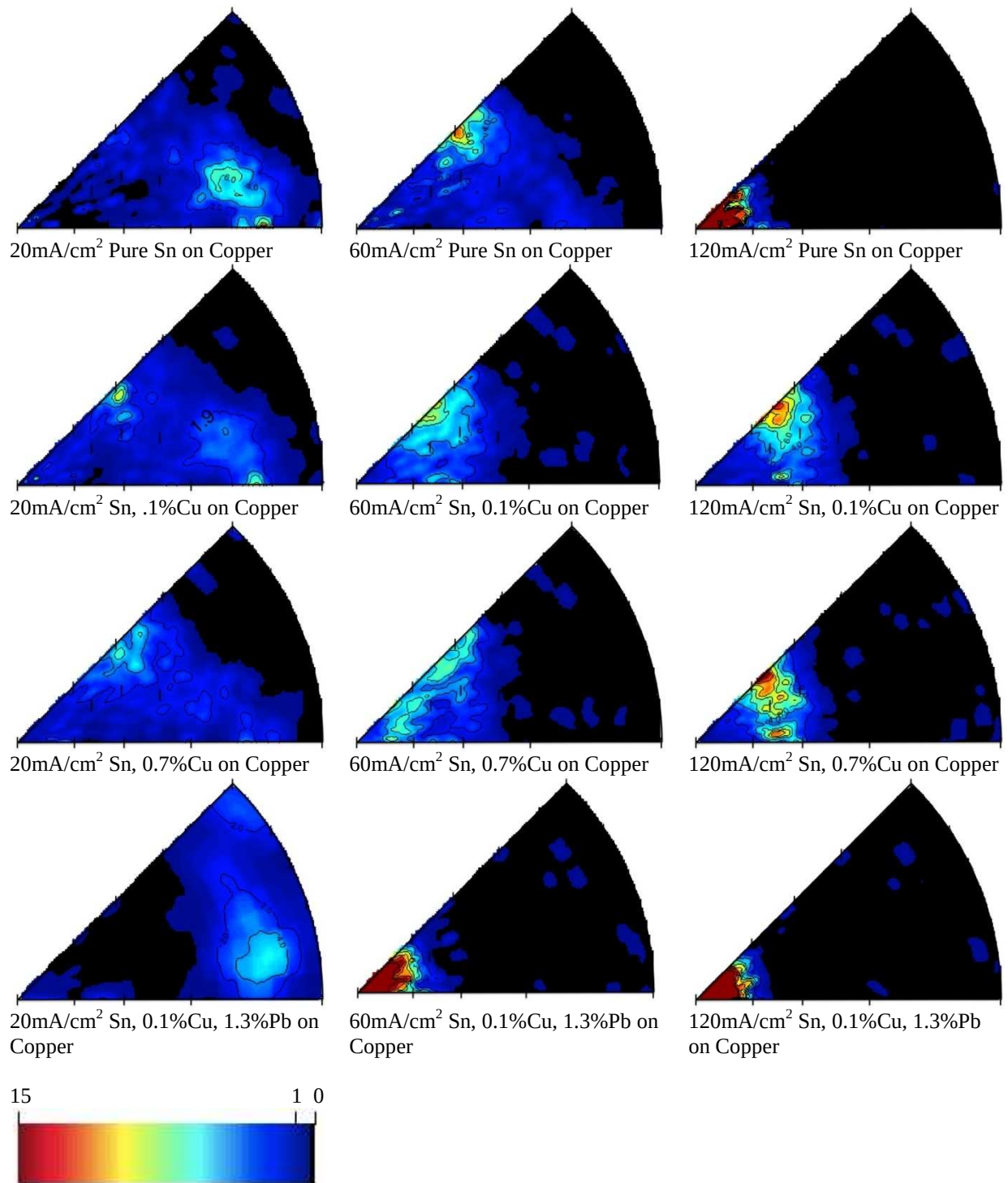


Figure 4: Equal area inverse pole figures with respect to sample normal showing crystallographic texture calculated for all films deposited on Cu.

Increasing current density for pure Sn resulted in a decrease between the c-axis and the film normal from 70° to being aligned with film normal and MRD's for the preferred orientations ranging from 12 to 105° . The largest change for the copper-containing films was the c-axis decreasing from 36 to 25° off the film normal with MRD's ranging from 7 to 17 for the preferred orientations.

Finally, depositing on bronze resulted in a preferred orientation with the c-axis being more aligned with the film normal for the Pb-free films. No significant texture differences were measured between the Sn, Cu, Pb films deposited on Cu and bronze. Also, the substrate effects on texture were not as strong as the effects measured for current density and electrolyte composition.

Microscopy

Defect density and type are shown in Table 1. It should be noted that the inspection time for the samples plated at $60\text{mA}/\text{cm}^2$ samples was 150 days, whereas the inspection time for the 20 and $120\text{mA}/\text{cm}^2$ samples was 60 days. The kinetics of defect formation therefore cannot be determined from the data in Table 1. There was a trend of increasing defect density with increasing current density with the exception of the $120\text{mA}/\text{cm}^2$ Sn, 0.1%Cu film deposited on Cu. All co-deposited Sn/Cu films on Cu exhibited whiskering with the exception of the $60\text{mA}/\text{cm}^2$ Sn, 0.1%Cu film. Films of Sn,Pb, Cu

deposited at 20 or $60\text{mA}/\text{cm}^2$ remained whisker-free, but films containing Pb deposited at $120\text{mA}/\text{cm}^2$ did whisker. Finally, Sn and Sn/Cu films deposited on phosphor bronze at $60\text{mA}/\text{cm}^2$ were all whisker free and had a low defect density of less than 30 defects per mm^2 .

Discussion

The analysis methods used for this study lead to quantitative crystallographic texture measurements. None of the measured films exhibited a random texture. The films had preferred orientations between the (111) and the (112). While this differs from other reported textures, it demonstrates that the electroplating conditions must be fully specified and the details of texture analysis must be considered to fully document the Sn films. For example, calculating texture using the measured intensity of a non-random sample versus a random sample only allows for the comparison of peaks measurable using XRD. Peaks for Sn such as the (111) are not measurable using XRD. This could be an influencing factor for the (321) texture results as the (321) is measurable using standard XRD.

Determining texture through inverse pole figures as opposed to pole figures is another advantage to using this technique. Using pole figure analysis requires that a pole figure be created for every Miller indices. If only low Miller indices such

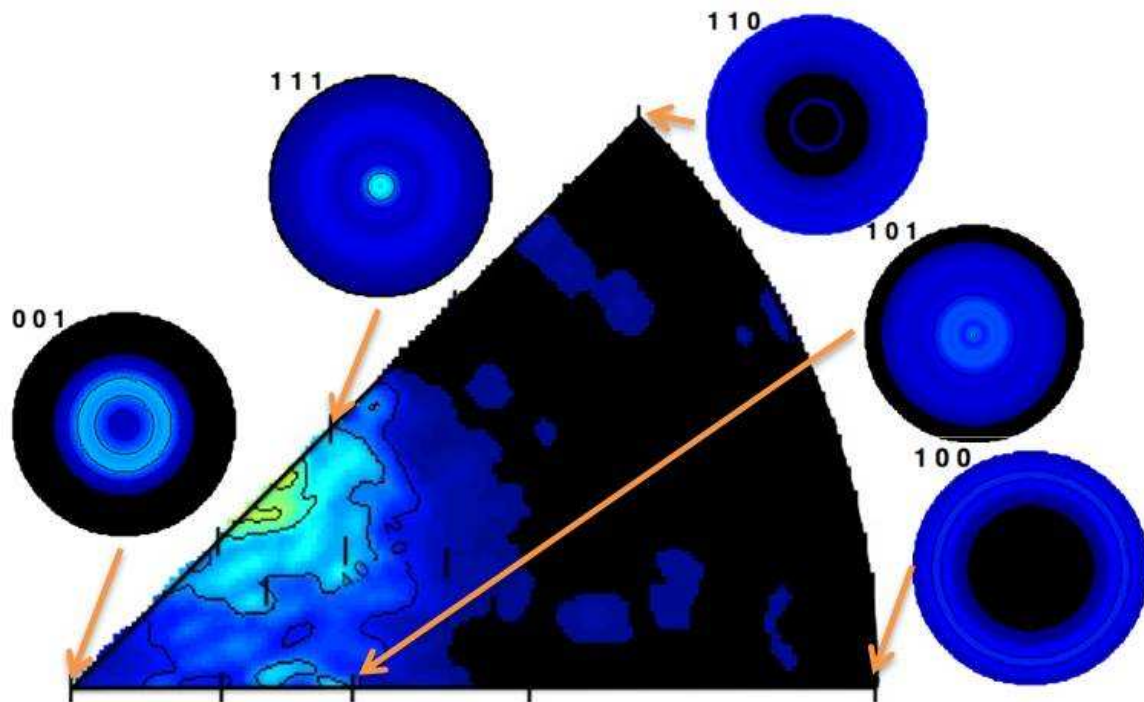


Figure 5: Inverse pole figure and pole figures for the $60\text{mA}/\text{cm}^2$ Sn, 0.1% Cu film on Cu showing possible problem with using pole figures to determine texture instead of inverse pole figures.

as the (001) or the (111) are evaluated, then potential high Miller indices preferred orientations will be missed. Figure 5 contains pole figures calculated for the 60mA/cm² Sn, 0.1%Cu film on Cu and compares the pole figures to the inverse pole figures. The low Miller index (111) appears to be the preferred orientation by using the calculated pole figures. The actual preferred orientation is the (445) with an MRD of 9.

Using this technique in a quality control environment could lead to better processes control and potential whisker detection. With respect to process control, this technique was capable of measuring texture differences due to current density and electrolyte chemistry. This method could also aid in whisker detection by showing changes in texture or MRD after thermal cycling. These changes are expected if grain growth occurs during thermal cycling. Furthermore, these measurements can be made in minutes by using XRD with GADDS as opposed to hours for grain by grain analysis techniques.

This technique also has applications in research and development. An understanding of why 1 in every 1000, 10,000, or more grains whisker is required for a fundamental understanding of the mechanisms behind whisker growth. Grain by grain analysis techniques such as synchrotron radiation or electron backscattered diffraction allows for micro-texture measurements of defects and surrounding grains. These micro-texture results of 1000's of grains can then be compared the macro-texture results of 100,000's of grains.

Incorporating this technique with JEDEC testing can add the value of the testing. The current testing outline in JESD201 takes weeks to complete and must be performed when a new process is used or a change in a current process is made. The testing returns a binary result – whether or not a particular film is whisker prone. Where this might be useful for evaluating the reliability concerns of the final product, more information regarding the material properties of the final product is needed for the development of whisker resistant deposits. By measuring texture before and after JEDEC thermal cycling can identify whisker prone textures and how texture changes for films with various propensities to whisker. Furthermore, this non-destructive analysis technique can be combined with other film characterization techniques or whisker detection testing. For example, film stress measurements can correlate texture to stress evolution. Ultimately, this technique is a tool in engineering a whisker resistant microstructure.

Trends were observed between texture and defect density and type. The propensity to whisker

increased as the angle between the preferred orientation c-axis and the film normal decreased. Current density effects were complicated by the time between plating and defect measurements. Samples plated at 60mA/cm² were evaluated at 150 days while samples plated at 20 and 120mA/cm² were evaluated at 60 days. Results did show the general trend of increasing current density leading to an increase in defect density and the MRD of the preferred orientation. The trends between defect density and type and texture are not without exception, but considering the number of factors that influence the propensity to whisker and limited number of systems evaluated the results are consistent. Quantitative crystallographic texture data will be essential in relating whisker propensity measurements across systems and in understanding the fundamental mechanisms of whisker growth.

Summary

A method for determining the quantitative crystallographic texture of Sn-based electroplated films was presented. This method combined XRD with GADSS with the Rietveld refinement program MAUD and is capable of detecting changes in texture due to current density, electrolyte chemistry, and substrate texture. This method has implications for quality control as well as research and development in the fundamental mechanisms in tin whisker growth. Combining this technique with other material characterization tools can aid in the development of whisker resistant engineered microstructures. For example, a trend toward increasing defect density was observed with increasing MRD and the MRD can be influenced with both current density and electrolyte composition.

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