The Surface Energies of β -Sn

—

A new Concept for Corrosion and Whisker Mitigation

P. Eckold^{[1],[2]}, M.S. Sellers^[3], R. Niewa^[1], W. Hgel^[2]

to be published in „Microelectronics Reliability“

- ^[1] University of Stuttgart, Institute of Inorganic Chemistry, Pfaffenwaldring 55, 70565 Stuttgart (Germany)
- ^[2] Robert Bosch GmbH, Automotive Electronics, 70442 Stuttgart (Germany)
- ^[3] Weapons and Materials Research Directorate, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD 21005 (United States of America)

E-mail: Pierre.Eckold@de.bosch.com

Phone: +49 711 811 43491

Key words: surface energy, tin corrosion, whisker, electrodeposition, EBSD analysis

Abstract

Corrosion data provided under high-temperature and high-humidity conditions as well as tin whisker growth studies are explained by differences in the surface energy of lattice planes within the crystal structure of β -tin. For this purpose, electrodeposited tin finishes were investigated regarding their microstructure utilizing X-ray diffraction, cross-sectional SEM and EBSD analysis. The corrosion as well as the tin whisker propensity strongly depends on the preferred orientation of the surface finishes. With an increasing texture along the (211) lattice plane a decreasing corrosion and whisker propensity was observed, in contrary, the presence of the (101) and (112) textures results in an increased corrosion and whisker propensity. The maximum whisker length was reduced by one order of magnitude by changing the preferred orientation towards the (211) lattice plane of the tin finish. Modified embedded-atom method simulations of tin surfaces demonstrate the minimization of the surface energy of (211) surfaces, whereas the surface energies of the (101) and (112) Miller planes are increased. We find a strong connection between the minimization of surface energy and the corrosion and tin whisker propensity of electrodeposited tin finishes. To our best knowledge, this is the first study connecting the influence of the electrodeposition parameters on the corrosion and whisker propensity explained by calculations of the surface energies of

the corresponding crystal faces. The applied parameters for electrodeposition influence the grain orientation and thus the surface energy of the tin layers which affects both the corrosion as well as the tin whisker propensity.

1 Introduction

Tin as a metal and in its alloys with copper and lead are widely used materials in different industrial branches. Prior 2003, tin-lead alloys were used as solder materials as well as surface finishes of components in electronic industries [1-5]. Soldering by using tin-lead based alloys and the existing substitutes was the method of choice attaching electronic components on a printed circuit board (PCB) during the manufacturing process of electronic assemblies. In order to promote “green manufacturing” in electronic industry the European Parliament and the European Council released a restriction of certain hazardous substances (RoHS) in electrical and electronic equipment in 2003 [6]. The industries concerned (e.g.: automotive industry) had to adapt production processes avoiding for example lead, cadmium or mercury as well as hexavalent chromium in their products. Accordingly, tin-lead alloys used as solder materials and surface finishes of electronic components had become unacceptable. To get an electronic component lead-free assembled on a printed circuit board, both the solder material and the metal finish of the component must not contain any lead [7-9]. The technical changeover of processes from tin-lead to lead-free assemblies was realized implementing lead-free solder materials (e.g. SAC305 [10]) as well as component finishes consisting of pure tin [11, 12]. The coating of connector finishes and component leads with pure tin is similar to the tin-lead process, thus the implementation of a completely new procedure was not necessary [13, 14]. Additional advantages of tin are its good solderability and its readily economical use. Despite acceptable properties of the new surface finish, the industry was confronted with a lot of reliability issues, like void formation [15, 16], cracks during thermal cycling [10, 17, 18], tin whisker growth [19-23] and corrosion under high-temperature and high-humidity conditions [24-27].

Tin whiskers are metallic, single crystalline filaments up to millimeters length and 1–10 μm in diameter, growing out of a metal layer due to mass transport towards the metal surface caused by compressive stress gradients [21]. This phenomenon is well-known for example for gold, cadmium, zinc and tin since the 1940s. There are four factors discussed in literature influencing the occurrence and the magnitude of compressive stress gradients in the metal layer. External forces, which appear in press-fit technologies result in compressive stress gradients and consequently in tin whisker growth. Even differences in the coefficient of

thermal expansion (CTE) between the substrate and the tin finish can lead to the formation of compressive and even tensile stress gradients caused by thermal cycling. Once a tin layer is formed on top of a copper type substrate material, copper atoms are diffusing within the tin layer to forming intermetallic compounds, like Cu_3Sn or Cu_6Sn_5 [23]. Due to the mass transport of copper into the tin layer, intermetallic phases between the substrate and the tin layer are formed particularly along the grain boundaries. This results in a pyramidal growth of the intermetallic compounds and to local volume expansions within the tin layer which leads to compressive stress gradients. Corrosion processes on tin surfaces as driving force for inducing compressive stress gradients are assumed. Corrosion intermediates and products located between columnar deposited grains of a tin surface seem to be responsible for stress states, which initiate whisker growth. Especially halides and flux residues located on the PCB after soldering processes are presumed to function as initiators for chemical reactions on the metal surface [22].

It is already known that chemical and physical properties of metallic or semi metallic layers are strongly influenced by the corresponding application process. In the case of the electrodeposition on tin, the adjusted plating parameters and the corresponding plating chemicals used, are responsible for emphasizing certain surface properties, like the microstructure [24, 28]. Plating parameters like the applied current density, the concentration of Sn^{2+} , the temperature of the electrolyte and its circulation around the specimens seem to be relevant variables influencing the resulting chemical and microstructural properties of the deposit [29]. There are few studies directly covering the impact of the crystallographic orientation on the corrosion and whisker propensity of electrodeposited tin coatings and the presented results are contradictory [30-32]. According to our results regarding the dependence of the corrosion propensity on the crystallographic orientation of electrodeposited tin finishes, we observed an increased resistance of tin surfaces against corrosion with an increased preferred orientation along the (211) and (321) Miller planes [24]. In addition, an increased corrosion propensity was detected with an increasing texture along the (101) and (112) lattice planes. Applying a simple structural model of the atomic arrangement within the corresponding tin surfaces was used to explain the observed behavior. For this purpose, simple bonding situations of un-relaxed surface atoms along the certain Miller planes were discussed. In addition, the influence of the electrodeposition parameters on the whisker propensity was recently studied by Ashworth et al. [29]. Changing the current density and the deposition thickness exhibited no change within the crystallographic orientation and thus no

significant differences in the whisker propensity were detected. These results indicate the strong influence of the specific plating chemicals used on the final properties of the deposit.

Additional work has shown a connection between tin surfaces and subsequent corrosion of tin finishes. According to conclusions within these computational and experimental studies, the surface energy of specific orientations of the metal lattice is shown to impact the behavior of both surface growth rate and finishes undergoing corrosion processes [33-36]. However, to our best knowledge, there is no study suggesting specific connections between surface energies of tin and the overall finish's corrosion and tin whisker propensities.

Within the present work, the influence of the texture on the corrosion and whisker propensity is explained by an analysis of the minimized surface energy, calculated by applying the modified embedded-atom method via molecular simulation – The evaluations of electron back-scattered diffraction (EBSD) and texture analyses provide information about the corresponding microstructures of the electrodeposited tin finishes. These results are correlated to the observed results from corrosion and whisker growth studies.

2 Experimental

2.1 Specimen preparation

Pure thin tin films, of 10 μm in layer thickness were electroplated on pure copper substrates (“Elekonta” PCB Cu platelets with dimensions: 1.0 cm $\times$ 2.0 cm $\times$ 1.6 mm) at room temperature using a commercial “matte-tin” electrolyte operating at different current densities within the electrolyte specification (5 – 25 A/dm²). The corresponding tin electrolyte was based on methanesulfonic acid and was used to be operated at 25 °C with a Sn²⁺ concentration of 70 g/l. Prior electrodeposition contaminations on the substrate material were removed applying a cathodic degreasing containing sodium silicate and an acidic etching bath, based on sodium persulfate. Electrodeposition experiments were carried out considering Faraday's law in order to generate the appropriate layer thickness. After the plating process residues of the acidic plating bath were removed by deionized water. The specimens were dried under nitrogen flush and subjected to a post bake treatment by annealing at 150 °C for one hour.

For EBSD analysis the electrodeposited tin finishes were embedded into a resin, where the tin surface was parallel to the polishing plane. Afterwards, the samples were manually ground down to the tin layer utilizing abrading media of 1 μm in grain size. The specimens were polished utilizing ion etching using Ar⁺ ions (4 keV, 180 μa) in order to generate a flat surface. For this purpose, the samples were mounted on a stage with an angle of 70 ° with

respect to the incident ion beam and polished for three minutes. Afterwards, a further polishing step applying 15 ° was performed.

For whisker experiments, industrial leadframe material with electrodeposited tin was used, demonstrating the concept of surface energy minimization, which can be utilized independent on the application process and its parameters. The plating chemistry of the industrial supplier remained the same.

2.2 Texture analysis

The crystallographic texture was analyzed using a “STOE STADI P” diffractometer with Mo $K_{\alpha 1}$ radiation (50 kV, 40 mA), equipped with a “Siemens ID 3003” generator, a Germanium (111) monochromator and a “DECTRIS MYTHEN 1K” detector in reflection geometry. The diffractometer was operated utilizing “WinXPOW” software, which was also used for baseline corrections. Additional software (“Origin 8.5”) was used to evaluate the data.

The evaluation of the diffraction data was carried out in accordance to literature data [24]. For this purpose the diffraction patterns were compared to the diffraction pattern of polycrystalline tin [37]. After normalization to the (312) reflection, the corresponding intensities of the significant reflections were compared with the calculated ones.

2.3 SEM and EBSD analysis conditions

Scanning electron micrographs were recorded using a “ZEISS EVO” scanning electron microscope equipped with three different detectors: a secondary electron detector, a solid state 4Q-BSD detector and energy dispersive X-ray spectrometer. Scanning electron micrographs were recorded applying an accelerating voltage of 15 kV, a probe current of 150 pA and working distances from 7 – 10 mm.

Electron back scattered diffraction was carried out on a “LEO 438VP” scanning electron microscope with an accelerating voltage of 20 kV and a probe current of 1.6 nA. The working distance was set to be 25 mm. The samples were placed with an angle of 70° with respect to the incident electron beam and scanned applying a scanning rate of 2 µm.

2.4 Calculation of surface energies

Slab configurations of atoms in the β -Sn lattice are created at different orientations to expose desired surface lattice planes using the Etomica molecular simulator [38]. An example of a slab configuration with the (220) surface exposed is shown in Fig. 1. Subsequent relaxation of the surface atoms was conducted with the LAMMPS molecular simulator using the Modified

Embedded Atom Method (MEAM) potential for tin [39, 40]. Further details about the MEAM potential and simulation specifics can be found in a previous work and references therein [33]. The LAMMPS simulation is configured as a two-dimensionally periodic simulation, where the slab extends in an infinite plane in the x - and y -directions and the two surfaces with a z -direction normal are exposed to a vacuum. The following equation is used to determine a single surface excess energy for relaxed and un-relaxed states [33, 41-42].

$$\gamma_s = \frac{E_{slab} - (E_{coh} \cdot N_{atoms})}{2 \cdot A} \quad (1)$$

In Equation (1), γ_s is the excess surface energy when compared to a bulk structure. E_{slab} is the energy of the system containing two surfaces, periodic in x and y . E_{coh} , the bulk cohesive energy (energy per atom), is multiplied by N_{atoms} , the number of atoms in our slab system. The numerator is divided by 2 to account for two surfaces, and is scaled by the area A of one surface. To relax the surfaces using LAMMPS, the potential energy of the entire configuration was minimized with respect to atomic positions using a conjugate gradient method. Configurations are built using minimum energy lattice constants, and in practice atoms at the center of the slab did not move, as they are in a bulk minimum energy configuration. Atoms at and near the surface of the slab do relax into locations that deviate from their original lattice site.

The amount of surface relaxation after minimization is quantified by computing the total squared displacement of all the atoms in the simulation and scaling this value by the surface area. As atoms in the center of the slab do not move during minimization, we believe this is a valid measurement to compare the relaxation of different surfaces, even if the configurations are slabs of different thicknesses. We refer to this quantity as the “surface relaxation factor”.

3 Results and Discussion

3.1 Excess Surface Energy Calculations

We computed the un-relaxed and relaxed excess surface energies for several surfaces of tin in the β -Sn crystal structure. Seven slabs, each with two surfaces, were constructed for the (101), (112), (200), (211), (220), (301), and (321) lattice planes and simulated according to the outlined methods in section 2.4. The excess surface energy was calculated for the static, un-relaxed, configuration as well as for the configuration relaxed with a conjugate gradient minimization of the potential energy. Additionally, the change in atomic position of surface atoms was quantified via the surface relaxation factor. These results are shown in Tab. 1. Of the seven surfaces modeled, the (211) surface has the smallest un-relaxed surface energy, and

the (220) has the largest un-relaxed surface energy. Upon minimization, all surfaces relax to a lower excess surface energy, with the (301) exhibiting the largest change, equal to $0.0055 \text{ eV/\AA}^2$. Interestingly, the (101) and (112) surfaces relax differently, and the ordering from smallest to largest excess surface energy changes. For the un-relaxed surfaces, the order of smallest to largest is (211), (200), (301), (101), (112), (321), (220). After relaxation however, the (112) surface becomes lower in energy than the (101) surface and the order changes to (211), (200), (301), (112), (101), (321), (220). It has to be pointed out that the lattice planes (101) and (301) exhibit nearly the same relaxation energies of about $5.5 \times 10^{-3} \text{ eV/\AA}^2$. The change in atomic positions during relaxation is quantified through a measure of the surface relaxation factor. Shown in Tab. 1 is a measure of this value for each surface. The surface atoms along the (321) lattice plane displace almost twice as much in length, whereas the degree of relaxation of the surface atoms along the (211) and (220) is only minute. However, there is no overall relationship between the energetic situation of the surface and the geometric relaxation factor. Fig. 2 shows a top and side view of the (211) and (321) slab with un-relaxed atoms in *red* and relaxed atoms in *blue*. Deviations from original atomic positions are evident in both views. The (211) surface, shown in Fig. 2, has minimal atomic displacement after relaxation, and relaxation occurs through shifts in lattice plane spacing near and normal to the surface. In general, the (211) lattice plane exhibits the smallest surface energy prior and after relaxation, in contrary, the (220) lattice plane offers the highest value for surface energy. In addition, surfaces orientated along (112) and (321) also provide comparably high values for surface energy. The minimized value in surface energy for surfaces orientated along the (211) lattice plane can be understood by an atomic model. Fig. 5 offers information about a distorted cubic-closed packing of tin atoms, which is supposed to be a favorable packing within a surface. Additionally, an atomic representation of the (220) surface is shown in Fig. 5. The fact of less interactions of surface atoms towards surface and bulk atoms may be translated to a weaker chemical bonding of the atoms in the (220) plane compared to atoms within the (211) lattice planes. According to these simple arguments, the (211) lattice plane should provide surfaces with a lower surface energy. In contrast, surfaces exhibiting a preferred orientation along (220) are presumed to exhibit high values for surface energy, which was supported by the simulations. However, the coverage of the surface by oxygen and the resulting existence of tin(IV) oxide and surface topologies are not implemented within these assumptions but prone to influence the energetic situation of the surfaces as well. Thus, this model is able to indicate tendencies rather to provide detailed information about surface reactivities.

3.2 Texture and EBSD Analysis of Electrodeposited Tin Finishes

In accordance to our previous research, a texture analysis of electrodeposited tin finishes with various layer thicknesses (2 – 15 μm) utilizing a matte tin electrolyte applying different current densities was carried out [24]. The results are illustrated in Fig. 3. In addition to the already presented data, the development of the intensity of the (211) reflection was additionally analyzed. From this data, it is obvious that the portion of tin grains orientated along the (220), (211) and (321) lattice planes is increased with an increasing layer thickness and current density. The maximum of the degree of preferred orientation is reached at a layer thickness of 10 μm applied with a current density of 15 A/dm^2 . Other lattice planes are almost not present on the metal surface.

It has to be pointed out that the average grain size does not change significantly over all current densities applied. With the help of SEM micrographs from cross sections an average grain diameter of $(5.02 \pm 0.2) \mu\text{m}$ was determined in agreement with our previous studies [24].

In order to analyze the presence of different orientated grains on the metal surface, EBSD analysis of certain tin surfaces was carried out. The stereographic projection of a tetragonal crystal indicates the position of the lattice planes along the amplitudes and longitudes. Due to a distinct surface roughness of electrodeposited tin finishes, the surface had to be prepared prior EBSD analysis. For this purpose, tin finishes of a layer thickness of 10 μm were electroplated on copper conductor material utilizing the tin electrolyte at 5, 10, 15 and 25 A/dm^2 . It has to be noted that the grain structure of the electrodeposited tin finishes was found to be columnar. The abrasion due to the polishing paper and the ion etching does not affect the orientation of the electrodeposited tin grains.

The results from EBSD analysis are shown in Fig. 4 and are consistent to the previous texture analysis of 10 μm tin finishes electrodeposited with the same matte tin electrolyte. The EBSD patterns indicate an increasing amount of the (211) lattice plane with increasing current density. With the program “ImageJ” [42] the amount of the violet colored (321) orientated grains was estimated for tin finishes electrodeposited with 15 and 25 A/dm^2 . For both, the ratio was about 8 % of the corresponding surface area. It has to be noted that an exact assignment of the lattice planes to the certain colors was not possible. However, according to the presented values for surface energies and the EBSD data, an overall decreased surface energy per surface area with an increasing current density can be determined, which was correlated with the increased ratio of the (211) lattice plane. A detailed view on the atomic

arrangement within the (211) lattice plane provides a possible explanation for its low surface energy (Fig. 5). The atomic arrangement orthogonal to the surface normal of the (211) lattice plane offers a distorted cubic-closed packing (*ccp*) of tin atoms, which provides the smallest surface energy, in comparison to other considered surfaces [33, 43].

3.3 Transfer to Corrosion Propensity

The general dependency of the corrosion propensity of electrodeposited tin finishes on the crystallographic orientation was previously investigated within our earlier studies, implementing detailed information about further influence factors like grain size distribution [24]. According to the presented detailed texture analysis, the corrosion propensity of an electrodeposited tin layer is strongly decreased by an increasing presence of tin grains orientated along the (211) and (321) lattice plane. The calculation of the surface energies of β -tin predicts that tin grains orientated along the (211) lattice plane would provide high resistance against metal corrosion. However, the simulations of the surfaces indicate a high corrosion propensity in case of a high ratio of tin grains orientated along the (321) lattice plane. The performed EBSD analysis indicates a negligible ratio of the tin grains orientated along the (321) lattice plane (Fig.4).

The crystallographic texture is a relative property of a surface, which always has to be compared to reference data, such as data from crystal structure determinations. The relative intensity of the (321) reflection in polycrystalline β -tin is $I_{(321)}/I_{(200)} = 16.969$ (I – reflection intensity) and thus the smallest value of the here considered reflections [37]. The intensity of the measured diffraction patterns was compared to the diffraction pattern of polycrystalline β -tin. Consequently, slight changes in the intensity of the (321) reflection leads to high/small values of relative intensity, which has been reported within the texture analysis (Fig. 3).

Thus, the corrosion propensity is strongly influenced by the degree of preferred orientation of tin grains along the (211) lattice plane. The distorted cubic-closed packing (*ccp*) of tin atoms perpendicular to the (211) plane supports this model. Thus, the corrosion propensity of an electrodeposited tin finish is related to the presence of tin grains orientated along the (211) lattice plane in β -tin. This microstructural property can be adjusted by the parameters during electrodeposition, as previously described within literature [24].

3.4 Transfer to Tin Whisker Propensity

As mentioned in the introduction, metal surfaces providing small surface energies may be able to relax compressive stress states [21, 22, 43-49]. In case of β -tin, the minimization of the surface energy due to optimized plating conditions would be a new strategy for tin whisker mitigation. For this purpose, several experiments inducing tin whisker growth at room temperature and under high-temperature and high-humidity conditions (80 °C / 80 % relative humidity) were carried out utilizing electrodeposited tin finishes with different preferred orientation.

From literature it is known, that grain boundary diffusion is the dominant transport mechanism promoting tin whisker growth caused by compressive stress gradients within the tin finish [50-52]. This does not significantly change varying the temperature from room temperature up to 80 °C. Changing the grain size distribution within the tin layer by changing the electrodeposition parameters (e.g. current density) would lead to a change in the grain boundary diffusivity and consequently in the tin whisker propensity especially in the growth rate. However, the grain size distribution of the specimens within this study was nearly remained constant, thus it was assumed that the grain boundary diffusivity was not significantly changed by changing the parameters of the electrodeposition process.

3.4.1 Tin Whisker Experiments at Room Temperature

Two leadframe strips were electrodeposited with 5 μm of tin utilizing industrial plating facilities of a supplier. The plating chemistry of the industrial suppliers was the same compared with the applied laboratory setup. Consequently, further plating parameters, e.g. bath geometry causes changes within the crystallographic texture. The control of single experimental parameters, like current density is not sufficient, since the overall focus has to be on the resulting preferred orientation, which depends on a multitude of different experimental parameters. The plating parameters were changed to generate different textured deposits. The data from the powder X-ray diffraction measurements are shown in Fig. 6 and the calculated ratios between the measured and simulated reflection intensities are shown in Tab. 2. The diffraction patterns of the leadframe strips differ in their preferred orientation. Both exhibit a preferred orientation along the (321) lattice plane, which is indicated by the strong intensity of the corresponding reflection. However, the tin finish of leadframe 1 provides a texture along the (211) lattice plane. In contrary, the intensity of the (211) reflection in leadframe 2 is decreased. It has to be pointed out that the samples were not annealed at 150 °C after the plating process. It is known from literature that the whisker propensity is strongly decreased by applying a post bake treatment [19, 45, 46]. The reason

not applying the post bake treatment was to distinguish between tin whisker growth caused by the generation of intermetallic phases and corrosion induced tin whisker growth. The effect of the grain orientation on the relaxation of compressive stress states and thus on the whisker propensity was investigated. Due to the absence of the post bake treatment a high whisker propensity was assumed. The irregular growth of intermetallic compounds, like Cu_6Sn_5 and the resulting compressive stress gradients within the tin finish should lead to significant whisker growth. The electrodeposited leadframe strips were exposed to air at room temperature for approximately one year. The analysis of whisker growth was carried out utilizing SEM. The corresponding results are illustrated in Fig. 7. From the multitude of measured SEM micrographs just two significant examples were chosen to demonstrate the difference in tin whisker propensity. As expected, it is obvious that both leadframe materials exhibit significant tin whisker growth. However, in case of leadframe 1 the whisker number and the average whisker length is significantly smaller compared to leadframe 2. The maximum whisker length on leadframe 1 is about 50 μm , and leadframe 2 exhibits tin whiskers longer than 200 μm . The considerable differences between the specimens were explained by the different grain orientations of the tin finish and the resulting minimized surface energies. The higher ratio of (211) lattice planes is responsible for the decrease of compressive stress gradients over the period of time und thus mitigates tin whisker growth.

3.4.2 Tin Whisker Experiments at High-Temperature and High-Humidity Conditions

In addition, further industrial manufactured leadframe strips were tested on their tin whisker propensity. For this purpose, the substrate material was electroplated with tin of approximately 10 μm in layer thickness applying two different electrodeposition processes. After the plating process the specimens were exposed to a post bake treatment (1 h, 150 °C) to avoid the irregular growth of intermetallic compounds. It has to be pointed out that the post bake treatment does not influence the preferred orientation of the tin surface. The reason applying the post bake treatment was to observe corrosion induced tin whisker growth instead of tin whisker growth caused by the irregular formation of IMCs along the grain boundaries. Afterwards powder X-ray diffraction measurements were carried out to analyze the crystallographic texture. The corresponding diffraction patterns are apparent in Fig. 8 and the calculated ratios between the measured and simulated reflection intensities are shown in Tab. 2. In accordance to previous shown PXRD investigations the preferred orientation of the two leadframe materials are strongly varying from each other. leadframe 3 exhibits a strong preferred orientation along the (211) and (321) lattice planes. In addition, a small (112) ratio

can be observed. In contrast, the texture of leadframe 4 (Fig. 8) is characterized by a strong orientation along (101) and (112). The electrodeposited and characterized leadframe materials were exposed to high-temperature and high-humidity conditions. For this purpose, the specimens were placed into the newly developed corrosion cells at 80 °C and 80 % relative humidity for 1000 h. Furthermore, the specimens were not contaminated with inorganic salts or organic contaminants, like fluxes. Comparable studies examine whisker lengths of a few micrometers [29]. Thus, the overall whisker propensity, including the whisker length and the whisker number were significantly decreased, compared to leadframes 1 and 2. Corresponding SEM micrographs of the tin surfaces of leadframe 3 and 4 confirmed this behavior (Fig. 9). The overall whisker length was decreased by approximately two orders of magnitude. In general, the beginning of tin whisker growth was observed. This may be explained by the presence of the passivation layer of tin(IV) oxide on top of the tin surfaces, which protects the tin layer from further corrosion. Contaminants, like halides would accelerate the corrosion rate. Thus, compressive stress gradients due to the increased formation of tin(II/IV) oxide would cause compressive stress states and consequently tin whisker growth. Within this experiment, exclusively the effect of the crystallographic orientation of the tin grains on the whisker propensity was studied, i.e. contamination was avoided. However, the comparison between leadframe 3 and leadframe 4 offers differences in the propensity of tin whisker growth. In accordance with the texture analysis, the whisker number is decreased by an increasing preferred orientation along the (211) lattice plane. The maximum whisker length on leadframe 3 was determined to be 5 μm . In contrast, on leadframe 4 tin whiskers of 22 μm could be observed. Even within this study, a reduced whisker propensity due to the selective application of the preferred orientation along the (211) lattice plane was observed. This indicates the minimization of the overall surface energy as a new strategy for whisker mitigation.

4 Conclusions

The generated data within this study provides a structural model of different β -tin surfaces regarding their microstructure and their surface energy. In relation to the presented corrosion data in [24] and the here shown tin whisker analyses the corrosion and tin whisker propensity of electrodeposited tin finishes strongly depends on the formation of low-energy surfaces, for example along the (211) lattice plane. In contrary to our previous work [24], the detailed microstructural analysis offered that the ratio of the (321) lattice plane was negligible. Surface energetic considerations indicate that a significant formation of tin grains along the (321)

lattice plane would increase the corrosion and whisker propensity of electrodeposited tin finishes.

The differences in the surface energies and the resulting corrosion and whisker propensities were explained by the atomic arrangement of the certain orientated tin surfaces, since atoms along the (211) lattice planes in β -tin are distorted cubic-closed packed. To our best knowledge this is the first study explaining the corrosion and tin whisker propensity by an extended crystallographic and energetic model of the tin surface, which might be implemented in industrial plating processes. We summarize the main points of the work below:

- 1) Experimental parameters of the plating process (e.g.: plating chemistry, current density, temperature of the electrolyte, electrolyte movement, sample and bath geometry, ...) strongly influence the orientation of the tin grains during the electrodeposited tin finish.
- 2) The orientation of the tin grains the resulting preferred orientation of the overall layer affects the excess energy of the surface as computationally presented. The (211) lattice plane provides the lowest surface energy, in contrary tin grains orientated along the (321) and (220) Miller planes exhibit high surface energy values.
- 3) A preferred orientation of grains within a tin surface along the (211) results in low corrosion and tin whisker propensity which was inversed by the occurrence of a preferred orientation along the (321) and (220) lattice plane.
- 4) Consequently, the plating parameters for each manufacturing process has to be adjusted according to the resulting preferred orientation of the resulting tin finish.

Future work has to be done controlling the crystallographic texture of an electrodeposited tin finish by an adjustment of the plating parameters, e.g. current density, electrolyte movement or temperature of the electrolyte.

5 Acknowledgements

The authors would like to thank the Robert Bosch GmbH for providing the financial support for this research. M.S. Sellers performed his portion of research independent of U.S. Army Research Laboratory interest and resources, and no financial support was provided by the U.S. Army Research Laboratory or any United States Government entity. In addition, we are deeply obliged to the electrolyte supplier for providing the required plating chemistries.

6 References

- [1] USGS - Tin Statistics and Information, Mineral Commodity Summaries (2010).
- [2] R. Darveaux, K. Banerji, Constitutive relations for tin-based solder joints, IEEE T. Compon. Hybr., 15 (1992) 1013-1024.
- [3] S. Knecht, L. Fox, Constitutive relation and creep-fatigue life model for eutectic tin-lead solder, IEEE T. Compon. Hybr., 13 (1990) 424-433.
- [4] Z. Mei, J.W. Morris, M.C. Shine, T.S.E. Summers, Effects of cooling rate on mechanical properties of near-eutectic tin-lead solder joints, J. Elec. Mater., 20 (1991) 599-608.
- [5] W.J. Plumbridge, Solders in electronics, J. Mater. Sci., 31 (1996) 2501-2514.
- [6] Directive 2002/95/EC, Official Journal of the European Union, Directive 2002/95/EC (2002) L37/19-L37/23.
- [7] M. Abtew, G. Selvaduray, Lead-free Solders in Microelectronics, Mater. Sci. Eng. R., 27 (2000) 95-141.
- [8] N.C. Lee, Getting Ready for Lead-free Solders*, Solder. Surf. Mt. Tech., 9 (1997) 65-69.
- [9] K.G. Snowdon, C.G. Tanner, J.R. Thompson, Lead free soldering electronic interconnect: Current status and future developments, 50th Electronic Components & Technology Conference 2000, pp. 1416-1419.
- [10] D. Herkommer, J. Punch, M. Reid, A reliability model for SAC solder covering isothermal mechanical cycling and thermal cycling conditions, Microelectron. Reliab., 50 (2010) 116-126.
- [11] T. Fang, M. Osterman, M. Pecht, Statistical analysis of tin whisker growth, Microelectron. Reliab., 46 (2006) 846-849.
- [12] K. Puttlitz, G. Galyon, Impact of the ROHS Directive on high-performance electronic systems, J. Mater. Sci., 18 (2007) 347-365.
- [13] C. Melton, H. Fuerhaupter, Lead-free Tin Surface Finish for PCB Assembly, Circuit World, 23 (1997) 30-31.
- [14] S.M. Ramkumar, R. Ghaffarian, A. Varanasi, Lead-free 0201 manufacturing, assembly and reliability test results, Microelectron. Reliab., 46 (2006) 244-262.
- [15] C.K. Chung, Y.J. Chen, W.M. Chen, C.R. Kao, Origin and evolution of voids in electroless Ni during soldering reaction, Acta Mater., 60 (2012) 4586-4593.
- [16] T. Ewald, Untersuchungen zum Mechanismus der Porenentstehung in Weichlotverbindungen beim Reflowlöten, Robert Bosch GmbH, Technische Universität Dresden, Templin, 2013.

- [17] X. Luhua, J.H.L. Pang, K.H. Prakash, T.H. Low, Isothermal and thermal cycling aging on IMC growth rate in lead-free and lead-based solder interface, *IEEE T Electron. Pack.*, 28 (2005) 408-414.
- [18] J.H.L. Pang, T.H. Low, B.S. Xiong, X. Luhua, C.C. Neo, Thermal cycling aging effects on Sn–Ag–Cu solder joint microstructure, IMC and strength, *Thin Solid Films*, 462–463 (2004) 370-375.
- [19] E. Chason, N. Jadhav, F. Pei, E. Buchovecky, A. Bower, Growth of whiskers from Sn surfaces: Driving forces and growth mechanisms, *Prog. Surf. Sci.*, 88 (2013) 103-131.
- [20] E.R. Crandall, Factors Governing Tin Whisker Growth, Graduate Faculty, Auburn University, Auburn, Alabama, 2012.
- [21] P. Oberndorff, M. Dittes, P. Crema, S. Chopin, Whisker Formation on Matte Sn Influencing of High Humidity, *Elec. Comp. C.*, 2005.
- [22] P. Oberndorff, M. Dittes, P. Crema, P. Su, E. Yu, Humidity Effects on Sn Whisker Formation, *IEEE T. Electron. Pack.*, 29 (2006) 239-245.
- [23] M. Soebich, M. Wohlschlögel, U. Welzel, E.J. Mittemeijer, W. Hügel, A. Seelkaamp, W. Liu, G.E. Ice, Local submicron strain gradients as the cause of Sn Whisker growth, *Appl. Phys.*, 94 (2009) 221901-221903.
- [24] P. Eckold, R. Niewa, W. Hügel, Texture of electrodeposited tin layers and its influence on their corrosion behavior, *Microelectron. Reliab.*, 54 (2014) 2578-2585.
- [25] B. Horvath, T. Shinohara, B. Illes, Corrosion properties of tin-copper alloy coatings in aspect of tin whisker growth, *J. Alloy. Compd.*, 577 (2013) 439-444.
- [26] L. Hua, C. Yang, Corrosion behavior, whisker growth, and electrochemical migration of Sn–3.0Ag–0.5Cu solder doping with In and Zn in NaCl solution, *Microelectron. Reliab.*, 51 (2011) 2274-2283.
- [27] D. Li, P.P. Conway, C. Liu, Corrosion characterization of tin-lead and lead free solders in 3.5 wt.% NaCl solution, *Corros. Sci.*, 50 (2008) 995-1004.
- [28] C. Zanella, S. Xing, F. Deflorian, Effect of electrodeposition parameters on chemical and morphological characteristics of Cu–Sn coatings from a methanesulfonic acid electrolyte, *Surf. Coat. Tech.*, 236 (2013) 394-399.
- [29] M.A. Ashworth, G.D. Wilcox, R.L. Higginson, R.J. Heath, C. Liu, R.J. Mortimer, The effect of electroplating parameters and substrate material on tin whisker formation, *Microelectron. Reliab.*, 55 (2015) 180-191.
- [30] W.E. Boggs, R.H. Kachik, G.E. Pellissier, The Effect of Crystallographic Orientation on the Oxidation of Tin, *J. Electrochem. Soc.*, 111 (1964) 636-646.

- [31] N. Pewnim, S. Roy, Electrodeposition of tin-rich Cu–Sn alloys from a methanesulfonic acid electrolyte, *Electrochim. Acta*, 90 (2013) 498-506.
- [32] S. Wen, J.A. Szpunar, Texture and Corrosion Resistance of Electrodeposited Tin Coatings, *Arch. Metall. Mater.*, 50 (2005) 175-180.
- [33] M.S. Sellers, A.J. Schultz, C. Basaran, D.A. Kofke, Atomistic modeling of β -Sn surface energies and adatom diffusivity, *Appl. Surf. Sci.*, 256 (2010) 4402-4407.
- [34] X. Zhong, G. Zhang, Y. Qiu, Z. Chen, X. Guo, C. Fu, The corrosion of tin under thin electrolyte layers containing chloride, *Corros. Sci.*, 66 (2013) 14-25.
- [35] A. Krupski, Growth of Sn on Mo(110) studied by AES and STM, *Surf. Sci.*, 605 (2011) 1291-1297.
- [36] A. Krupski, Growth morphology of thin films on metallic and oxide surfaces, *J. Phys.: Condensed Matter*, 26 (2014) 053001.
- [37] H.E. Swanson, E. Tatge, Standard x-ray diffraction powder patterns, *Natl. Bureau of Standards*, 539 (1953) 1-95.
- [38] A.J. Schultz, D.A. Kofke, Etomica: An object-oriented framework for molecular simulation, *J. Comput. Chem.*, 36 (2015) 573-583.
- [39] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, *J. Comput. Phys.*, 117 (1995) 1-19.
- [40] LAMMPS Simulator, <http://lammps.sandia.gov>, (2009).
- [41] M. Zhao, W. Zheng, J. Li, Z. Wen, M. Gu, C.Q. Sun: Atomistic origin, temperature dependence, and responsibilities of surface energies: An extended broken-bond rule, *Phys. Rev. B.*, 75 (2007) 085427.
- [42] J.-M. Zhang, F. Ma, K.-W. Xu, Calculation of the surface energy of FCC metals with modified embedded-atom method, *Appl. Surf. Sci.*, 229 (2004) 34-42.
- [43] ImageJ, W. Rasband, National Institute of Health, USA.
- [44] Z. Jie-Hua, P. Su, D. Min, S. Chopin, P.S. Ho, Microstructure-Based Stress Modeling of Tin Whisker Growth, *IEEE T. Electron. Pack.*, 29 (2006) 265-273.
- [45] U. Lindborg, Observations on the growth of whisker crystals from zinc electroplate, *Metall. Trans. A*, 6 (1975) 1581-1586.
- [46] Y. Mizuguchi, Y. Murakami, S. Tomiya, T. Asai, T. Kiga, K. Suganuma, Effect of Crystal Orientation on Mechanically Induced Sn Whiskers on Sn-Cu Plating, *J. Elec. Mater.*, 41 (2012) 1859-1867.

- [47] P. Snugovsky, S. Meschter, Z. Bagheri, E. Kosiba, M. Romansky, J. Kennedy, Whisker Formation Induced by Component and Assembly Ionic Contamination, *J. Elec. Mater.*, 41 (2012) 204-223.
- [48] M. Sobiech, J. Teufel, U. Welzel, E.J. Mittemeijer, W. Hgel, Stress Relaxation Mechanisms of Sn and SnPb Coatings Electrodeposited on Cu: Avoidance of Whiskering, *J. Elec. Mater.*, 40 (2011) 2300-2313.
- [49] R. Schetty, Minimization of tin whisker formation for lead-free electronics finishing, *Circuit World*, 27 (2001) 17-20.
- [50] K.N. Tu, Irreversible processes of spontaneous whisker growth in bimetallic Cu-Sn thin-film reactions, *Phys. Rev. B*, 49 (1994) 2030-2034.
- [51] K.N. Tu, J.C.M. Li, Spontaneous whisker growth on lead-free solder finishes, *Mater. Sci. Eng. A*, 409 (2005) 131-139.
- [52] J. Smetana, Theory of Tin Whisker Growth - The End Game, *IEEE T. Electron. Pack.*, 30 (2007) 11-22.

Figures and Tables

Fig. 1: Rendering of a slab of tin in the β -Sn lattice configuration with the un-relaxed (220) surface exposed on the top and bottom (not visible). *Dark* atoms are the simulated atomic configuration, *light* atoms are replicas extending in the $+x$ and $+y$ directions to indicate periodicity resembling an infinite plane.

Fig. 2: Illustration of the differences between the initial (blue) and relaxed (red) positions of Sn atoms within the simulated slabs along the lattice planes (321) and (211) in side and top view mode.

Fig. 3: Texture analysis of electrodeposited tin finishes on copper conductor material using a commercial matte tin electrolyte. No differences between the measured and the simulated reflection intensity would result in a value of 1 in relative intensity, which indicates no texture along the certain lattice plane. Higher / lower values in relative intensity indicate a preferred presence / absence in the corresponding reflection intensity. Slight changes in process parameters lead to errors in relative intensity of ± 0.5 .

Fig. 4: EBSD analysis showing the effect of deposition current density (**a**) 5 A/dm², **b**) 10 A/dm², **c**) 15 A/dm², **d**) 25 A/dm²) on the orientation of 10 µm tin deposits on copper conductor material (top). Surface normal-projected inverse pole figure orientation maps and corresponding folded inverse pole figures contour maps showing the surface normal orientation. Legend and pole figure information of the stereographic projection of a tetragonal crystal (bottom).

Fig. 5: Sections of the tetragonal crystal structure of β -tin viewed **top)** along the (211) lattice plane **middle)** orthogonal to the (211) lattice plane and **bottom)** along the (220) lattice plane.

Fig. 6: Powder X-ray diffraction patterns of the electrodeposited tin finishes on leadframe 1 and 2 compared with the simulated diffraction pattern of β -tin.

Fig. 7: SEM micrographs showing typical whisker densities on leadframe 1 (a and b) leadframe 2 (c and d). Highlighted areas demonstrate significant tin whisker growth.

Fig. 8: Powder X-ray diffraction patterns of the electrodeposited tin finishes on leadframes 3 and 4 compared with the simulated diffraction pattern of β -tin.

Fig. 9: SEM micrographs showing typical whisker densities on leadframe 3 (a and b) and leadframe 4 (c and d). Highlighted areas demonstrate significant tin whisker growth.

Tab. 1: Computed un-relaxed and relaxed surface energies for various β -Sn lattice planes, and the surface relaxation factor.

(hkl)	$\gamma_s / \text{eV}/\text{\AA}^2$ un-relaxed	$\gamma_s / \text{eV}/\text{\AA}^2$ relaxed	$\Delta \gamma_s / 10^{-3} \text{eV}/\text{\AA}^2$ (un-relaxed – relaxed)	relaxation factor / $\text{\AA}^2/\text{\AA}^2$
101	0.0569	0.0535	5.5	0.0079
112	0.0570	0.0516	5.4	0.0262
200	0.0496	0.0459	3.7	0.0364
211	0.0467	0.0443	2.4	0.0070
220	0.0622	0.0618	0.4	0.0002
301	0.0560	0.0505	5.5	0.0134
321	0.0612	0.0559	5.3	0.0506

Tab. 2: Ratios of measured ($I_{\text{measurement}}$) and simulated ($I_{\text{simulated}}$) reflection intensities of specific miller planes for leadframe 1 – 4.

Leadframe	$I_{\text{measurement}}/I_{\text{simulated}} (hkl)$									
	(200)	(101)	(202)	(211)	(301)	(112)	(400)	(321)	(420)	(411)
1	0.08	0.19	2.08	1.24	1.21	0.24	0.34	5.22	1.00	2.35
2	–	0.05	0.72	0.72	0.30	0.14	0.22	5.23	0.43	1.01
3	0.07	0.05	0.15	1.54	–	1.88	–	2.85	–	0.40
4	–	0.69	0.20	0.08	–	5.22	–	0.14	–	0.51