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Texture of electrodeposited tin layers and its influence on their corrosion behavior

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ABSTRACT

Differences in the degree of corrosion of pure thin tin films electrodeposited on copper substrates were investigated in dependence on the layer thickness and the texture of the tin layers. The change of the preferred orientation of the tin layer deposited by applying different current densities was analyzed using X-ray diffraction. A graphical evaluation was used to determine the degree of corrosion after sample exposition to NaCl contaminations and humidity. Results show that a preferred orientation along the lattice planes (3 2 1) and (2 2 0) enhances the corrosion resistance of the tin layer by about one order of magnitude compared to a non-textured sample based on the corroded area. In contrast, a texture along (1 0 1) and (1 1 2) accelerates the oxidation of tin by a factor of about three to four compared with a randomly orientated specimen. The corrosion dependence on the preferred orientation decreases with increasing layer thickness. Moreover, scanning electron micrographs show no effect to the size of the tin grains on variations of the current density. In summary, changes in the process parameters of the electrodeposition lead to a variation of texture and thus modify the chemical and corrosion properties of the resulting tin layers. Consequently reliability properties like solderability or whisker growth in further applications depend on these parameters.

1. Introduction

In order to promote "green manufacturing" in electronic industry the European Parliament and the European Council released a restriction of the use of certain hazardous substances in electrical and electronic equipment in 2003 [1]. The industries concerned (e.g.: automotive industry) had to adapt production processes to avoid 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. Lead–free solders are well implemented in industry [2,3]. Tin–silver–copper (SAC) solders and tin–copper for hot air solder leveling are commonly used types of solder materials in electronic industry [4,5]. The influence on the solder joint reliability of the intermetallic compound, which is formed during the soldering process, is well studied [6,7]. The effort of the last few years was the development of better solder materials in terms of reducing the growth of the intermetallic compound or lower soldering temperatures. This was realized with the help of additional dopants, like bismuth [8,9].

The replacement of tin–lead alloys as surface finishes is more challenging. The obvious alternative was the use of pure tin finishes [10,11]. The coating of connector finishes and component leads with pure tin is similar to the tin–lead process, thus implementation of a completely new procedure was not necessary. Other advantages of tin are its good solderability and its readily economical use [12]. Despite acceptable properties of the new surface finish the industry was confronted with a lot of other reliability issues, like void formation [13] whisker growth [12,14,15], and corrosion of the tin finish under high temperature and high humidity conditions [16,17]. Extensive studies show a different grade of whisker growth by investigating different electronic components [18]. It has to be taken into account that differences in the manufacturing process of the specific electronic component (e.g. supplier, plating parameters) can result in different testing results. Corrosion processes as driving force for inducing stress gradients to promote whisker growth is known in literature, but not widely understood [16]. Future work will focus on the investigation and the influence of corrosion intermediates and products on tin whisker growth. It is well studied that the chemical properties of a metal coating depends on the texture,

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the microstructure (e.g. amount and distribution of grain boundaries) and the composition of the deposit [19]. For example, the corrosion resistance of zinc coatings with a strong basal texture is superior to those with less basal orientation [20]. The key to intentionally cause such specific chemical properties of metal finishes is the applied electrochemical plating process. It is well known that a variety of different process parameters exist which influence the chemical and physical properties of the metal finish [21]. Variation of the substrate material leads to a change in texture and morphology of the metal layer, while a change of the sample orientation with respect to the anode leads to changes in the electric field, applied which results in fluctuations of layer thicknesses [22]. The temperature of the electrolyte and its circulation around the specimens are further parameters which influence the resulting metal finish and its chemical properties.

The driving force for a chemical reaction is the change of the free energy from the initial to the final state. Different arrangements of atoms on a surface finish caused by changing the grain orientation lead to a change in the free energy of the surface, the initial state [23,24]. This change in energy can contribute in a decisive manner to the kinetics of reactions occurring on the metal surface during corrosion processes [25].

In the present work the influence of the texture on the corrosion resistance of electrodeposited tin layers was studied. Three commercial tin electrolytes were used to investigate the correlation between the current density applied and the resulting texture of the tin layer.

2. Experimental

2.1. Specimen preparation

Pure thin Sn films, with layer thicknesses of 2, 5, 10 and 15 μm were electroplated on pure Cu substrates (“Elekonta” PCB Cu platelets with dimensions: 1.0 cm × 2.0 cm × 1.6 mm) at room temperature using three commercial “matte-tin” electrolytes (Table 1) and different current densities within and beyond the electrolyte specification (from 5 to 35 A/dm^2).

Contaminations on the Cu substrates were removed by using a basic cathodic degreasing containing sodium silicate and an acidic etching bath, based on sodium persulfate. After the plating process the specimens were washed with deionized water and dried with nitrogen flush. The specimens were subjected to a post-bake treatment directly after layer deposition by annealing the specimens for 1 h at 150 °C in air. The resulting thickness and the microstructure of the Sn films were determined with scanning electron microscopy (SEM) images of cross sections prepared by grinding, polishing, ion etching and sputtering the samples with gold. The micrographs were recorded using a “ZEISS EVO” scanning electron microscope equipped with three different detectors: a secondary electron detector, a solid state 4Q-SBD detector and an energy dispersive X-ray detector.

Table 1
Overview about the tin electrolytes used for electrodeposition.

Electrolyte No.	Type	$c(Sn^{2+})$/g/l	Operating ranges
1	Matte, methanesulfonic acid	70	5–25 A/dm^2, 25–45 °C
2	Matte, methanesulfonic acid	60	10–20 A/dm^2, 25–55 °C
3	Matte, methanesulfonic acid	25	0.5–5 A/dm^2, 25–35 °C

2.2. Texture analysis

The texture analysis of the resulting tin layers was carried out using X-ray diffraction. Three samples obtained with each experimental parameter set were measured. The measurements were performed applying a “STOE STADI P” diffractometer with Mo Kα_1 radiation (50 kV, 40 mA), equipped with a Siemens ID 3003 generator, a Germanium (111) monochromator and a “DECTRIS MYTHEN 1K” detector. The specimens were mounted on top of a reflection stage and the measurements were performed applying an incidence angle of 3°. During the measurements the samples were rotating orthogonal to the surface normal. The diffractometer was operated utilizing “WinXPOW” software, which was also used for a baseline correction. Additional software (“Origin 8.5”) was used to evaluate the data. Three ranges of each sample were measured and added for further analyzing.

The resulting diffraction patterns were compared with a diffraction pattern of non textured polycrystalline tin calculated from the crystal structure data of tin [26]. The measured diffraction patterns were normalized to the (312) reflections of the calculated powder pattern of tin. To determine preferred orientations of the specimens the intensities of the significant reflexes (200), (101), (220), (112) and (321) were compared with the calculated ones. The use of integrated intensities instead of absolute intensities leads to basically identical results.

2.3. Contamination and corrosion

To create a consistent level of contamination the specimens were immerged for 20 min into a 0.1 M sodium chloride salt solution. Afterwards the samples were dried at air.

In order to ensure constant humidity conditions the temperature dependent vapor pressure of an aqueous saturated potassium bromide solution was employed. To induce the corrosion process the specimens were mounted on a specimen holder in a glass chamber filled with the saturated potassium bromide salt solution and exposed for 200 h at 80 °C and 80% relative humidity. After the exposition the samples were removed and investigated with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Furthermore, the level of corrosion of each sample was investigated by calculating the corroded area from the local blackening of the tin finish (“ImageJ” software).

3. Results and discussion

3.1. Texture analysis

The crystallographic texture or the preferred orientation can be described as the distribution of crystallographic orientations in a polycrystalline sample. That means, texture as relative property has always to be compared with reference data. The reflection intensities of simulated diffraction patterns calculated from crystal structure data supply the required information.

It is known that the substrate material influences the growth mechanism of electrodeposited metal finishes. Often the texture of the substrate is adopted by the electroplated metal finish, which is called epitaxy [27]. In order to reduce this effect, a copper conductor material was used for electrodeposition of tin. This material provides a nearly non-textured copper surface, which was checked utilizing X-ray diffraction (Fig. 1). The diffraction pattern of the conductor material and the simulated pattern from crystal structure data [26] were normalized to the (111) reflection of copper. The differences in the reflection intensities of the measured and the calculated diffraction patterns are insignificant, which indicates the basically non-textured character of the copper