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Mitigation of tin whisker growth by inserting Ni nanocones

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ABSTRACT

An innovative controllable way has been proposed to mitigate tin whisker growth by inserting Ni nanocones prepared by electrodeposition. The results reveal that, after inserting Ni nanocones, tin whisker formation is mitigated effectively for 1.6 μm Sn coating but there is no inhibition effect for 4.5 μm Sn coating. The coatings are characterized by X-ray diffraction, scanning electron microscopy, energy dispersive spectrometer and electron backscatter diffraction (EBSD). The EBSD results show that Sn grain size without Ni nanocones increases significantly after indentation test compared with Sn grains with Ni nanocones. The inhibition effect of Ni nanocones on whisker growth can be ascribed to its specific structure which prevents dynamic recrystallization and produces horizontal grain boundaries of Sn grains. The structural inhibition method and mechanism proposed are of great importance to the research of tin whisker.

1. Introduction

Tin whisker has been a threat in terms of electronics reliability for several decades. Electrodeposited Sn coatings are used extensively in various sectors of the electronics industry due to its favorable performance such as contact resistance, corrosion resistance and solderability [1]. However, tin whiskers are easy to form on the surface of Sn coatings, which will cause short circuits and device failures [2]. Moreover, with the increasing demand for electronics miniaturization, tin whisker growth is still a severe threat to reliability of microelectronic devices [3]. To understand the formation mechanism of tin whisker, many theories, including oxidation [4], recrystallization [5,6], and stress [7] and others [8] have been proposed, but there is no theory that can explain all phenomenon.

However, it is generally accepted that compressive stress is the primary driving force for tin whisker growth [9]. Therefore, several effective mitigation methods, such as conformal coatings [10], Ni barrier layers [11] and Pb or Bi alloying [12,13], have been developed, which can reduce compressive stress to some extent but there are many difficulties to be overcome. Conformal coating might be an effective way to prevent tin whisker growth by reducing the oxidation of Sn coatings, but it is hard to ensure the long-term effectiveness. Ni barrier layer can suppress the formation of tin whisker to some extent because it can induce tensile stress and prevent the formation of IMCs (intermetallic compounds) [11], but it has no noticeable inhibitory effect on whisker growth under temperature cycling or elevated temperature/humidity conditions [14]. Pb was used to suppress tin whisker in the past, but it has been forbidden by the RoHS (Restriction of Hazardous Substances) since 2006 due to its toxicity. Alloying Bi is an effect way to decrease stress, but excessive Bi will embrittle Sn-based solders, and whether Bi does no harm to human body and the environment is not yet clear. Therefore, it may not be a wise choice to inhibit the growth of tin whiskers.

In fact, compressive stress and the diffusion of Sn atom are two key factors for suppressing the formation of tin whisker. Therefore, relaxing stress of Sn coatings is still an effective way to mitigate whisker growth. Pb and Bi can change grain structure from columnar to equi-axed and in this way stress of Sn coating is relaxed significantly [13]. And horizontal grain boundaries play an important role in stress relaxation [9]. At the same time, Sn whisker formation is closely related to dislocations [15,16] and thus preventing dislocation motion can suppress the formation of tin whisker. Nevertheless, there is scarce literature on the use of micro-nano structures to inhibit the formation of tin whiskers. In this paper, we proposed a new method to suppress the formation of tin whiskers by using Ni nanocones structure that was inserted between Cu alloy and Sn layer. Ni nanocones structure can prevent the motion of dislocations in Sn grains, and meanwhile produce horizontal grain boundaries to relax stress. Micro-indentation test was used to accelerate the growth of tin whisker, and the effects of Ni nanocones on tin whisker were investigated. Moreover, electron backscatter diffraction was used to analyze the effects of Ni nanocones on Sn grain and the structural inhibition mechanism of tin whisker was proposed.

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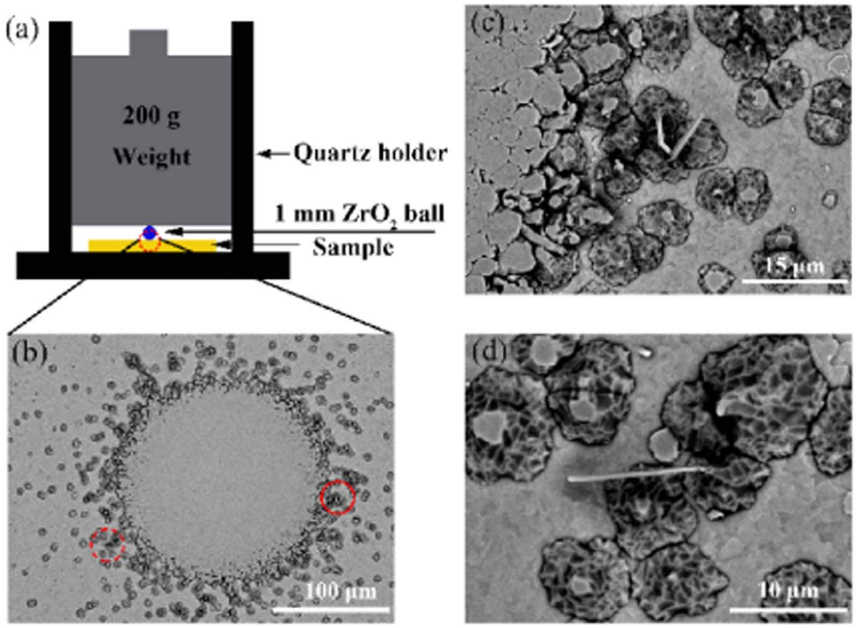

Fig. 1. (a) Schematic of indentation device. SEM images of (b) micro-indentation and (c, d) Sn whiskers at the edge of micro-indentation; (c) and (d) show areas of the solid line circle and the dashed line circle in figure (b) respectively.

2. Experimental Procedures

Cu alloy (Cu-2.3Fe-0.12Zn-0.03P wt%) was used as substrates and cut into required size. All substrates were pretreated by electrochemically degreasing, 20% H_2SO_4 cleaning and washed by deionized water. Then Ni nanocones was electrodeposited on the Cu alloy at 2.0 Adm^{-2} and 50 °C for 15 min. The electrolyte was composed of analytical pure H_3BO_3 (0.5 mol/L), $NiCl_2 \cdot 6H_2O$ (1.0 mol/L), and crystal modifier of ethylenediamine dihydrochloride (1.5 mol/L), as reported by Hang et al. [17]. By contrast, Ni plane layer was also electrodeposited on the Cu alloy at 4.0 Adm^{-2} and 50 °C for 3 min. The nickel electrolyte was composed of analytical pure H_3BO_3 (0.5 mol/L), $NiSO_4 \cdot 6H_2O$ (1.0 mol/L), $NiCl_2 \cdot 6H_2O$ (0.16 mol/L), Sodium Saccharin (0.004 mol/L), 1,4-butynediol (0.005 mol/L) and Sodium dodecyl sulfate (0.001 mol/L). Finally, the bright Sn films were electrodeposited on the Ni nanocones and Ni plane layer respectively at 1.0 Adm^{-2} and 25 °C. Thus, two types of samples with different Sn thickness, including Sn/Ni/Cu and Sn/Ni cones/Cu, were prepared.

Micro-indentation test [18] was used to accelerate the growth of tin whiskers through a constant compressive force. As is shown in Fig. 1a, the device consists of a 200 g weight, a 1 mm ZrO_2 ball and a quartz holder that can fix the weight in a horizontal position and the sample is on the bottom of the holder. The devices were placed in the clean room where the temperature and relative humidity were 20–25 °C and 40–50% respectively. The period of indentation test was 5 days. A micro-indentation was obtained on the Sn coatings (e.g., Fig. 1b) and tin whiskers formed at the edge of micro-indentation (e.g., Fig.1c, e). Five of each type of samples were used for statistical analysis and tin whiskers longer than 5 μm were counted.

The morphology of the Ni nanocones was characterized by field emitting scan electronic microscope (FE-SEM, FEI SIRION 200). The backscattered electron (BSE) imaging and EBSD analysis were characterized by low vacuum scanning electron microscope (LV-SEM, FEI NOVA NanoSEM 230). EBSD was conducted at an accelerated voltage of 20 kV and high-resolution maps were obtained with a step size of 0.04 μm. The length and width of the scanning area were 5 μm. Sn whiskers were also observed by scan electronic microscope (Hitachi TM3000). Energy dispersive spectrometer (EDS) was used to investigate the element distribution. X-ray diffraction pattern was recorded from 25° to 85°, using Rigaku D/MAX-IIIA X-ray polycrystaline diffractometer with Cu K_α radiation (λ = 0.15418 nm).

3. Results and Discussion

3.1. Surface and Cross-sectional Morphology

The morphology of and Ni nanocones was observed by FE-SEM, as shown in Fig. 2a–b. Ni nanocones of tower shape are uniformly distributed and perpendicular to the surface of the substrate. It is measured that the mean height is about 700 nm and the mean root diameter is 500 nm. Fig. 2c–f show cross-sectional SEM images of samples of Sn/Ni/Cu and Sn/Ni cones/Cu. The interfaces of Sn layer and Ni (or Ni cones) layer show no voids and Ni nanocones are embedded into Sn layer. Two different thicknesses of Sn layer were measured to be about 1.6 μm (Fig. 2c and d) and 4.5 μm (Fig. 2e and f) respectively. The Sn, Ag and Cu elements line scan of Sn/Ni/Cu and Sn/Ni cones/Cu was characterized by EDS, as shown in Fig. 2e and f.

3.2. Whisker Results

After indentation test, whiskers or hillocks formed around the indentations. The indentation morphology of samples Sn/Ni/Cu (Fig. 3a and c) and Sn/Ni cones/Cu (Fig. 3b and d) was shown in Fig. 3. Obviously, the whiskers and hillocks of sample Sn/Ni/Cu are more than sample Sn/Ni cones/Cu. Moreover, hillocks of sample Sn/Ni/Cu formed even in the distance from the edge of the indentation, while hillocks of sample Sn/Ni cones/Cu formed only near the edge of the indentation. The morphology of whiskers and hillocks are shown in Fig. 3e and f, respectively. The results indicate that whiskers and hillocks are suppressed significantly under the pressure after inserting Ni nanocones layer.

Table 1 shows the results whisker statistics of two types of samples after micro-indentation. Five of each type sample were used for indentation test and whisker parameters including maximum length, mean length, maximum diameter, mean diameter and amount were counted. The results show that the length and density of tin whiskers forming on 1.6 μm Sn coating decreases dramatically after inserting Ni nanocones, which indicates that Ni nanocones have noticeable inhibitory effect on tin whisker formation. However, for 4.5 μm Sn coatings, whisker length and density are approximately the same. The results show that Ni nanocones have few effect on whisker formation, when Sn coating thickens.