

A Mechanism for Hillock Formation over Electrodeposited Thin Tin Films

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Abstract

Tin films of one micron thickness were electroplated over a silicon wafer pre-coated with an adhesion layer of chromium followed by a layer of nickel; both layers were deposited by evaporation. A special sample holder was designed to apply compressive stresses in the electroplated tin film. After an annealing period in vacuum at 160°C for 7 days, hillocks 10-30µm diameter and 30-150µm height grew with a density about 7 per square mm. On the top of the hillocks there appeared a polycrystalline layer similar to the original tin film. The FIB technique determined the underlying hillock microstructure to be single crystals of tin with a[001] direction perpendicular to the film. It is proposed that the mass transport of tin atoms to hillocks (an likely whiskers) occurred by a fluid-flow, fast diffusion mechanism along the tin-nickel interface .

Key Words: tin whiskers, tin hillocks, growth mechanism, flow path, FIB

Introduction

In the early years of the microelectronics industry, the concern of tin whiskers growing from tin coatings was an important problem. The literature was reviewed recently by Galyon and Palmer [1]. The problem was mitigated by electroplating tin-lead (tin with 3-10% lead by weight) alloys instead of pure tin as described by Arnold [2] The mechanism was not clearly understood. However in recent years, environmental regulations such as Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) have limited the use of lead in electronics. Because the most cost-effective surface finish for electronic parts is 100% tin, this problem of tin whiskers has appeared, again.

Several early landmark studies have shed some light on possible mechanisms. Koonce and Arnold in 1954 [3] showed that the growth was from the base and not from the top by observing that the tip morphology was unchanged while the whisker grew longer. Fisher et al. [4] in 1954 found that a compressive stress of 52 MPa could accelerate the whisker growth to 1 micron per sec at room temperature which was a rate that was too fast to have been supported by lattice (bulk) diffusion. Baker [5] in 1957 showed that the base of the whisker was usually a grain boundary or an interface boundary inconsistent with a dislocation mechanism. Lindborg [6] in 1975 used x-ray

diffraction to determine stresses in electroplated films and showed that a minimum stress level was required for the initiation of whisker growth.

Recent studies have provided further insight into the tin whisker mechanism. Tu [7] in 1994 suggested that the oxide layer on the tin coating must be broken to allow the whisker to grow. Lee and Lee [8] in 1998 measured the residual stresses in tin films on copper substrates and found that the 11MPa tensile stress, which occurred in the as deposited layer, changed to 8 MPa compressive after storage about 5 days. Lee and Lee also identified a thickness effect. They observed that 60 whiskers per mm^2 grew from a tin film thickness of 1 micron. The whisker density decreased continuously to 20 whiskers per mm^2 for a tin thickness of 4.5 microns. In 2001 Zhang et al [9-12] used the focused ion beam (FIB) technique and found that the root of the whisker was close to intermetallic particles projecting upwards from the tin/substrate interface, implying that the accelerated growth of whiskers for tin on copper was caused by the tin-copper interface reaction. Choi et al [13,14] used micro-focus x-ray diffraction from a synchrotron source to find that the stress surrounding the whisker area was more compressive than the remaining tin coating area and that the whisker grain had a different orientation (210) than the surrounding grains (321). Boettinger et al. [15] measured and analyzed the residual stress development in tin, tin-copper and tin-lead layers electrodeposited on phosphor bronze cantilever beams and observed whisker and hillock formation. Tu and Li [16] introduced the idea that grain boundary fluid flow may be faster than grain boundary diffusion. This idea comes from a comparison between self diffusion and viscous flow in liquids [17].

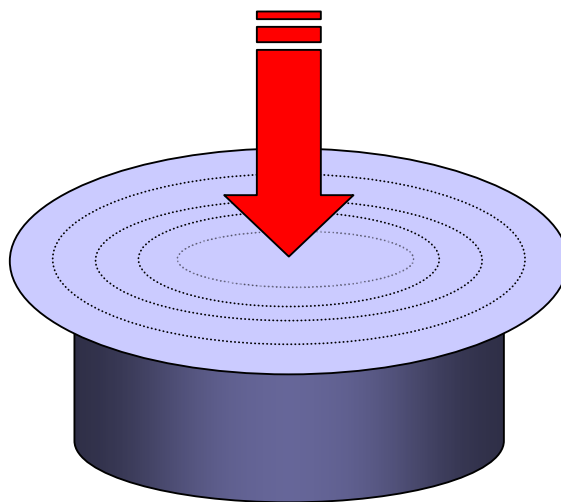
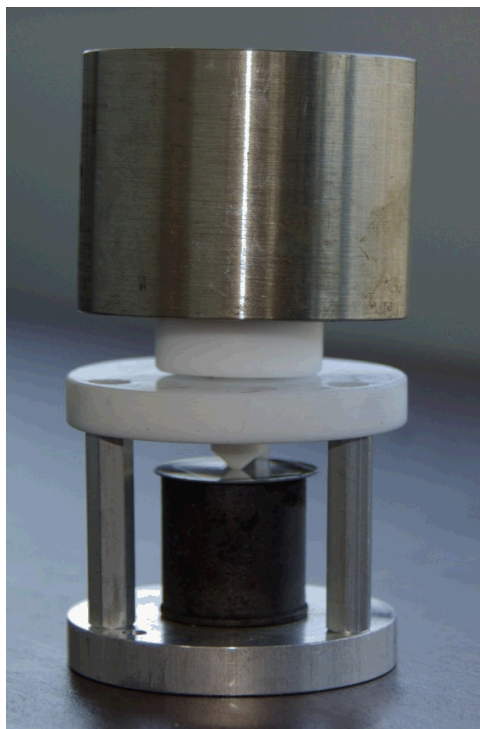
More recently, Woodrow [18] did a delicate experiment by plating one layer of isotope tin¹¹⁸ on a brass coupon, then covered by another layer of isotope tin¹²⁰. A larger area of tin¹²⁰ was plated over than that of tin¹¹⁸ so that, in the middle, there were the two layers of the two isotopes surrounded by a single layer of tin¹²⁰. After some time, in the whiskers grown in the single layer area, tin¹¹⁸ was also found there. Since almost all the grain boundaries were perpendicular to the surface, the author concluded that diffusion of tin atoms must have taken place along the interface of copper and tin unless the atoms could move above or under the oxide layer, which was deemed unlikely. Williams et al. [19] electrolytically deposited 15 micron of tin -copper alloy (1.4-3.7w/oCu) onto a W substrate and found hillocks on the tin layers and whiskers on tin-copper layers. The purpose of this experiment was to show that it is not necessary to form intermetallic compounds with the substrate to induce whisker formation. But they did not rule out the possibility of residual stress from the electroplating contributing to whisker development.

Since the driving force for whisker development is generally accepted to be a compressive stress, an experiment was developed in the present study that applied a known compressive stress on a silicon wafer coated with tin. The goal of this study was to determine whether the tin/substrate interface is a path for very fast tin diffusion that is needed to support hillock growth in the time frame that the latter takes place. The tin layer would be only one grain thick, thereby eliminating the effects of horizontal grain

boundaries, that is, boundaries parallel to the coating surface.

Experimental

In most industrial applications, tin films are electroplated onto copper-based substrate. Most research to date has examined such systems [7-8, 13-16]. Unfortunately, the stress is unknown and/or cannot be well controlled. Also, there are local stress effects caused by interface reactions between tin and copper. In order to investigate tin hillocks and whiskers with the goal of finding the responsible mechanism, it is necessary to eliminate the interface reactions variable. Therefore, the tin films were electroplated on silicon wafers so that a more accurately known compressive stress could be applied to the film. A sample holder was designed for this purpose as shown in Fig.1. The tin-coated silicon wafer was on the upper surface. The wafer was loaded in the center and supported below around the edge to create biaxial compressive stresses in the tin film (Fig.2). This compressive stress distribution can be calculated analytically. For example, a 500g load applied at the center will create a hydrostatic stress of 10 MPa at 5 mm from the center.



↑ Fig. 2 The circular Si wafer with a tin coating on the upper surface is bent by a constant force loaded at the center

← Fig. 1 Sample holder with a dead weight

The substrate was a one-inch diameter n-type silicon wafer with an [100] orientation and a thickness of 350 μm . One-side was optically polished. A 15nm-thick chromium layer was evaporated on the polished side, followed by a 200nm-thick nickel layer to serve as adhesion layers. Then, a commercial electrolyte was used for electroplating the matte tin layer, using a current density of 10A/sq.ft or 108 A/m². The final thickness of the tin film was 1 μm with grain size of 2-3 μm .

The tin-coated silicon wafer was put in the sample holder as described earlier with a 500g dead load applied at the center. The whole assembly was placed in a vacuum oven maintained at 160 C and around 10^{-4} Torr for seven days in order to grow whiskers.

After the heating treatment, the sample's surface was observed in a scanning electron microscope (SEM) for whisker development. Focused ion beam (FIB) cross sectioning was used to cut through the tin film in order to observe the underlying microstructure of film and the hillocks. A FIB-fabricated sample was also separated and etched with 10% hydrochloride acid for 15 seconds to provide a TEM sample. It took over 60 hours to prepare one TEM sample of the large hillock. The final thickness of the TEM sample was 180nm.

Results

SEM observations revealed that after seven days at temperature, many large hillocks appeared on the surface of the 1 μm thick film (Figs. 3 and 4). These hillocks had diameters 10-30 μm and lengths of 30-150 μm . Although the image in Fig. 3 could be labeled a "whisker", it was termed a hillock due to its large diameter relative to that of typical tin whiskers (1 – 5 μm). These hillocks looked very curvy in appearance, having rough lines on the surface along the growth direction. The average distance between two hillocks was about 400 μm .

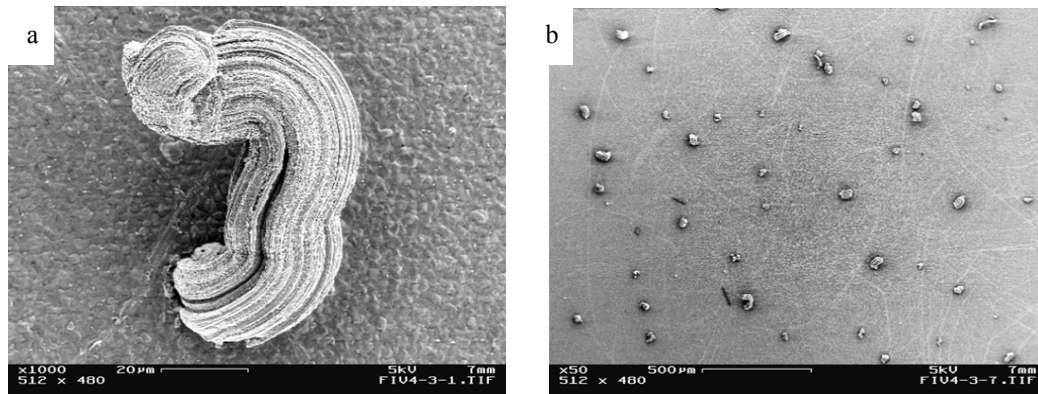


Fig.3 (a) a hillock of 25 μm diameter and over 100 μm long (b) Density of hillocks about 7 per mm^2

At a higher magnification, the top of the hillock appeared to be covered by a polycrystalline layer similar to the surface structure of the tin film, namely grains of diameters of 2-3 μm . That thickness of the top surface layer was one micron thick, which was also similar to the original tin layer thickness. See Fig. 4.

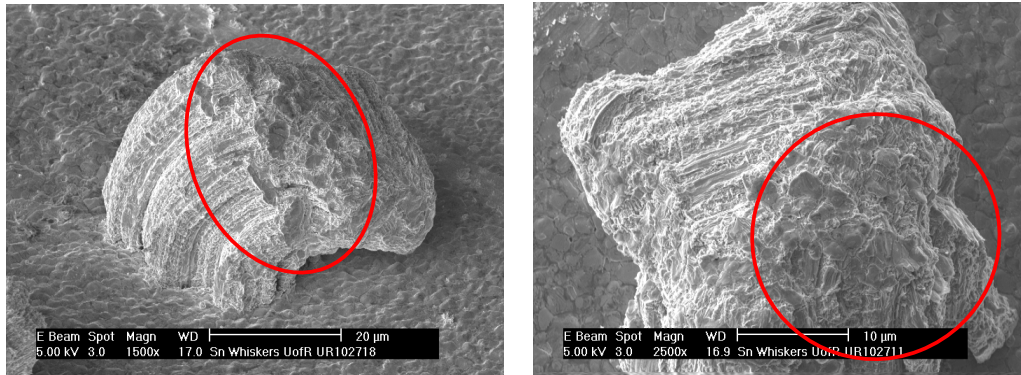


Fig.4 A polycrystalline layer with 2-3 μm grain size was found on the top of hillocks

After etching in 10% HCl for 15s, this layer was partially removed, exposing the internal microstructure. The exposed tin appeared to be a single crystal because no grain boundaries were observed (Fig.5).

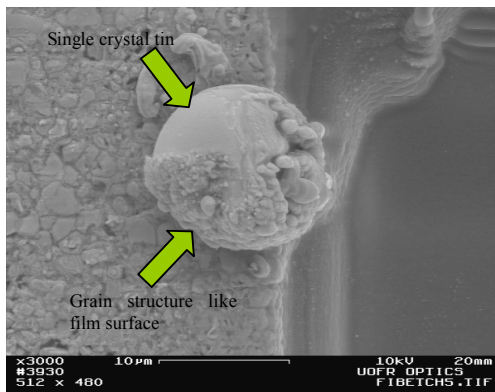


Fig.5 A hillock etched by 10% HCl for 15s.

In order to confirm that the large hillock was a single crystal, a TEM sample was fabricated using the FIB technique. Fig.6(a) shows the platinum coating before the FIB cutting was performed. Fig.6(b) is the unfinished section of TEM sample. The “skin” on top of the hillock was 1 μm , which is the same as the thickness of tin film. When the TEM sample was finished, it was lifted up by static force as shown in Fig.7(c). The top of this TEM sample was lost by gallium ion beam etching process during the final FIB cutting.

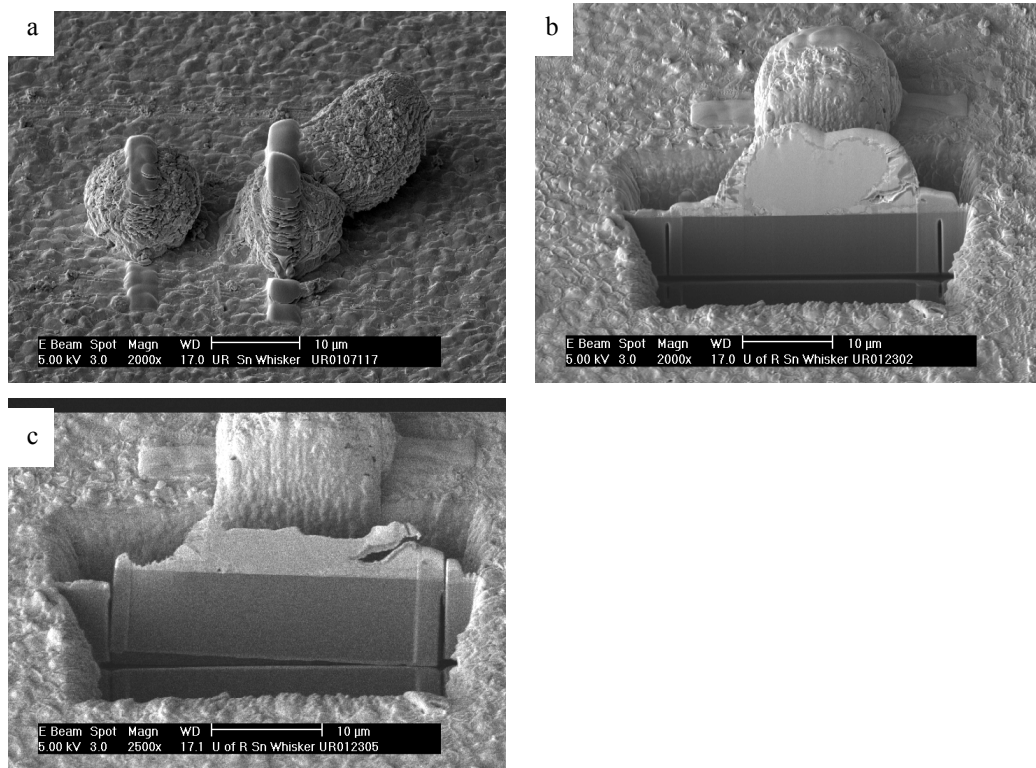
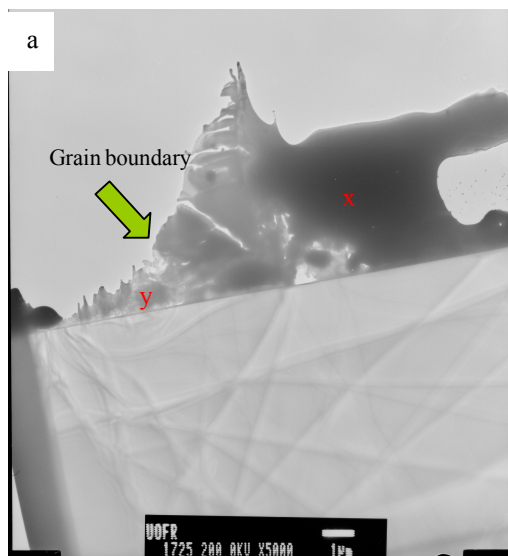


Fig.6 FIB fabricated TEM sample

The image in Fig.7(a) shows the hillock's morphology under TEM. Some melting of the TEM sample occurred under the electron microscope beam. Nevertheless, several observations were made. Grain x in Fig.7(a) is the hillock, grain y is next to the hillock. Fig.7(b-c) are the diffraction patterns of grain x and y. The analysis of TEM diffraction pattern was listed in Table 1. Results show that the randomly-selected large hillock was a single crystal with orientation of $[001]$. The neighboring grain had an orientation of $[-1 -1 3]$.



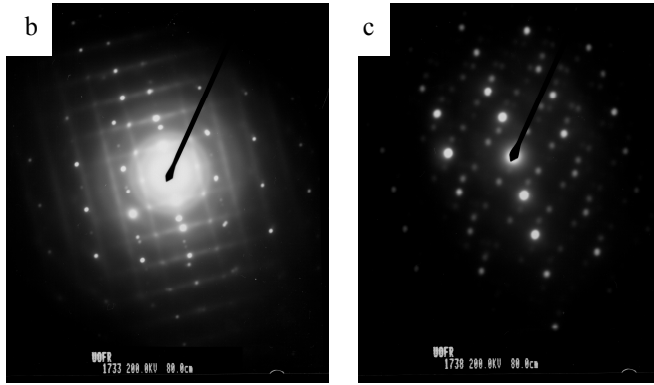


Fig.7 (a) A hillock TEM image (b-c) Diffraction patterns of grain x and y, respectively

Table 1 Grain orientation analysis

Grain	R (cm)	d (10^{-10} m)	(hkl)	Orientation of grain
Hillock (a)	0.6750	2.9630	2 0 0	[0 0 1]
	0.6786	2.9472	0 2 0	
	0.9500	2.1053	2 2 0	
Neighboring grain (b)	0.9375	2.1333	2 -2 0	[-1 -1 3]
	1.2667	1.5789	0 3 1	
	1.6750	1.9400	2 1 1	

The FIB technique also revealed the lateral microstructure of tin film. The grain boundaries were perpendicular to the film as expected. No horizontal boundaries were present in this film. However, many voids were present at the grain boundaries; those are the black dots on the walls (Fig.8).

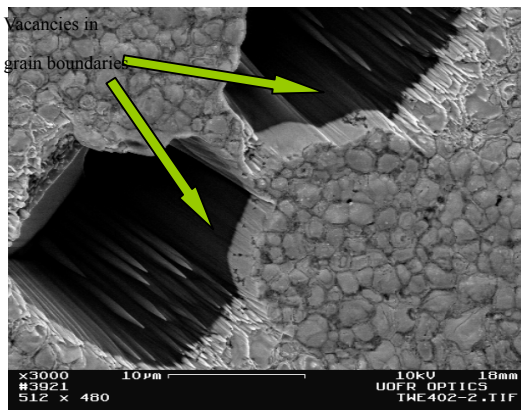


Fig.8 Perpendicular boundaries in 1 μ m thick tin film, sample tilting angle: 30°

Fig.9 shows a hillock that was cross sectioned by the FIB cut. First, it was noticed that the tin layer thickness surrounding the hillock was uniform; there were no obvious

concave or sinking areas. Secondly, the bottom of the hillock was integral to the tin layer. That is, there was no demarcation that separated the hillock structure from the original tin film. (The chromium and nickel layers were too thin to be observed.)

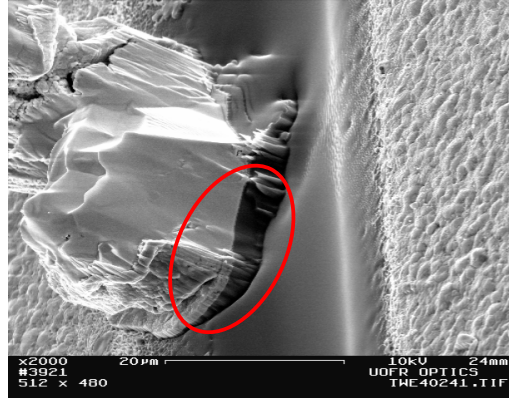


Fig.9 FIB-cut large hillock

Discussion

In the case of these large hillocks, their average diameter is $20\mu\text{m}$ and the average length $50\mu\text{m}$, so the average volume, as calculated from $V=\pi r^2 h$ with $r = 10\mu\text{m}$, $h = 50\mu\text{m}$, is equal to $1.6 \times 10^4 \mu\text{m}^3$. In an area of 3.5 mm^2 (Fig.3(d)), the total number of large hillocks is 25, or 7 per mm^2 in density. So the average distance between two hillocks is $375\mu\text{m}$. The total volume of hillocks is $1.12 \times 10^5 \mu\text{m}^3$ in a square mm and the volume of tin film is $10^6 \mu\text{m}^3$. Thus, the volume of hillocks is 11.2% of the deposited tin layer. For each hillock the average growth rate is $0.026 \mu\text{m}^3/\text{sec}$ in volume, or $8.28 \times 10^{-5} \mu\text{m}/\text{sec}$ in length, on average. The mechanism that supports this rapid mass transport is described below.

Fig.8 shows many vertical grain boundaries in the tin layer. These boundaries are under compressive stress due to the bending of the silicon wafer. Such compressive stress will increase the chemical potential of tin in the tin-tin grain boundaries to cause the tin to diffuse rapidly along those boundaries, arriving at the tin-nickel interface. The tin atoms in the grain boundaries are continuously supplied from the neighboring grains. If it is assumed that diffusion along the tin-tin boundaries is faster compared to the growth rate of hillocks, then hillock growth is controlled by mass transport along the tin-nickel interface. The following analysis will explore this presumption and hypothesize on the diffusion process along the latter interface.

Fig.4 shows that the microstructure on top of hillock was the same as the deposited tin layer. The thickness was also the same, about $1\mu\text{m}$. Fig.5 shows a clear boundary between the top layer and the bulk hillock, which was a single crystal. Lastly, Fig.9 shows that the hillock sat directly on the tin-nickel interface instead of atop the tin layer. All of these images indicated that the hillock grew from the interface between the original tin

layer and the nickel layer. This point implies that, tin atoms were transported along the tin-nickel interface.

Fig.10 is a schematic diagram that illustrates the proposed growth process of hillocks. Tin atoms are transported along the tin-nickel interface. Those atoms support the growth of those grains having the preferred orientation of [001]. This is a slow process and may explain the incubation period observed in hillock (and whisker) growth. There is no stress gradient around the whisker as yet so that the macro-compressive stress along with thermal activation provided the driving force for tin diffusion. When each of these preferred grains grows large enough to lift the interface and break the surrounding oxide layer, a hillock is created that is stress free, thereby creating a stress gradient that further enhances its development. The hillock growth is now much faster than that at nucleation stage, will continue until the stress gradient was exhausted.

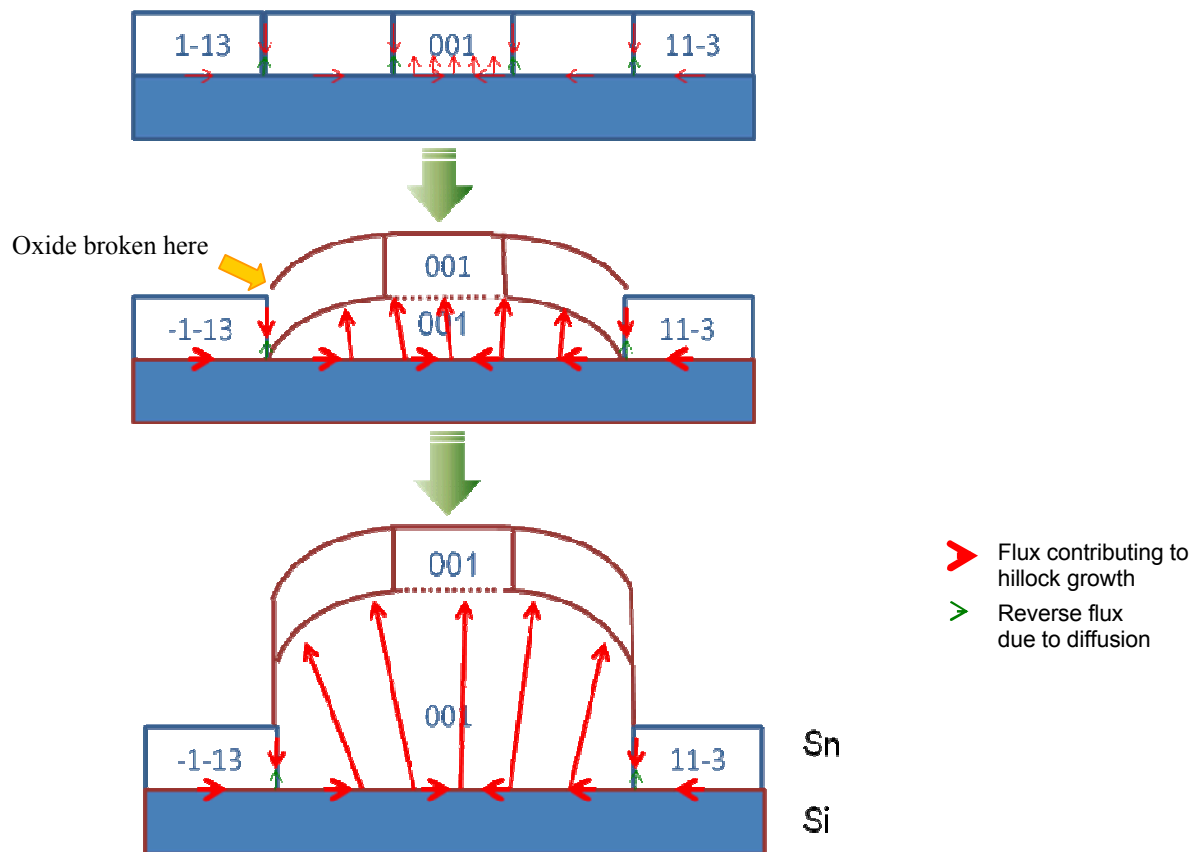


Fig.10 Hillock nucleation and growth

Calculation based on the interface transport

Atomic transport by interface boundary fluid flow mechanism, rather than the slower

grain boundary diffusion mechanism, has been introduced to explain whisker growth [16]. In the present study, this theory is extended to the tin-nickel interface. As the rate controlling step, the tin atoms diffuse along the tin-nickel interface in order to reach the bottom of the hillocks. Therefore, a fast-diffusion mechanism, based on the fluid flow hypothesis, is suspected of occurring along the tin-nickel interface.

An analogy to this hypothesis is that of impression creep and the associated viscous (layer) flow as described by Chen and Li [20]. In that work, the cylindrical indenter of radius a provides a pressure p . The indenter sinks in with a velocity V and the atoms move away radially in viscous flow. At the steady state, the pressure distribution or gradient drives mass transport in the viscous layer.

In the case of hillocks, the viscous layer at the tin-nickel interface is under pressure resulting from the applied load. Once formed, the cylindrical hillock of radius a becomes stress free. The tin atoms flow along the tin-nickel interface of thickness h to the root of the hillock. Under the presumed pressure gradient, the following equation calculates the growth rate, V :

$$V = \frac{2ph^3}{8\eta a^2} \quad (1)$$

If V is 8.28×10^{-5} micron per sec, p is 10 MPa, h is 1 nm, a is 10 micron, then the viscosity is calculated to be 0.302 Pa-s. This value is two orders of magnitude higher than 0.0025 Pa-s for liquid tin [21], when the latter was hypothetically extrapolated to 160 C. (Of course, the bulk melting temperature of tin is 232°C. This extrapolation would refer to atomic movements of a few layers.) Yet, this value of 0.302 Pa-s may be sufficient to explain the rapid growth of hillocks (and presumably, tin whiskers). The following calculation demonstrates this point. The Einstein equation establishes a relation between viscosity and self-diffusivity:

$$\frac{D\eta}{kT} = \frac{1}{2\pi\Omega^{1/3}} \quad (2)$$

where D is self diffusivity in m^2/s , η is viscosity in Pa-s, k is Boltzmann constant,

1.38×10^{-23} J/atom $^\circ\text{K}$, T is absolute temperature (433 K) in $^\circ\text{K}$ and Ω is atomic volume in m^3/atom (for tin, it is 0.0275 nm^3). The self diffusivity is calculated to be $1.04 \times 10^{-11} \text{ m}^2/\text{s}$. This value is approximately three orders of magnitude faster than self-diffusivity of tin in polycrystalline tin, $3 \times 10^{-14} \text{ m}^2/\text{s}$ extrapolated to 160 C from Pawlicki's data [22]. Because self-diffusion was measured in a polycrystalline sample, both bulk and grain boundary diffusion mechanisms were active. See also a collection of self diffusion data and discussion by Yang and Li [23]. These calculations provide evidence of a fast transport process, here described as a interface viscous flow mechanism, that supports the growth of hillocks under the present test conditions. The specific microstructural construct that provides the fast diffusion path may be a consequence of the interface reaction between tin and nickel. Tin diffuses into nickel faster than nickel into tin [11, 12].

Therefore, there may exist an excess of vacancies on the tin side of the interface that support the fast, fluid-flow like transport of tin along the tin-nickel boundary.

Conclusion

A 1 μm thick, electroplated tin layer was exposed to a mechanically applied compressive stress by bending a silicon wafer coated with it. The nickel and chromium underlayers provided adhesion as well as eliminated local residual stress effects generated by large-scale interface reactions. Whisker growth was promoted by heat treating the samples at 160 C for 7 days under a 500 g load. The result was the formation of large hillocks at a density of about 7 per mm^2 . Within the tin layer, the grain boundaries were oriented almost exclusively perpendicular to the film. The grain size was 2-3 μm .

The large hillocks were single crystals covered with a layer of polycrystalline tin that was the as-deposited layer. The nucleation of the hillock initiated from a previously existing grain, which had the favored oriented grain, for example, the [001] direction. The hillock grew from the interface between tin and nickel, not from the surface of the tin coating.

Assuming the hillock to be stress free, but surrounded by a tin layer that was under a compressive stress, the tin atoms flowed along the interface between tin and nickel layers toward the root of the hillock. The overall scenario is similar to that of impression creep. Therefore, using the equations developed for impression creep, the calculated viscosity associated with hillock growth, indicated a self-diffusivity that was considerably faster than that observed in polycrystalline tin at 160 C, thereby providing further evidence that a fast diffusion mechanism based upon the interface viscous flow model, was a possible process for this phenomenon.

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