Driving Force and Mechanism for Spontaneous Metal Whisker Formation

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The room temperature spontaneous growth of low melting point metal whiskers, such as Sn, poses a serious reliability problem in the semiconducting industry; a problem that has become acute with the introduction of Pb-free technology. To date, this 50+ year old problem has resisted interpretation. Herein we show that the driving force is essentially a reaction between oxygen and the sprouting metal. The resulting volume expansion creates a compressive stress that pushes the whiskers up. The model proposed explains our observations on In and Sn whiskers and many past observations. The solution is in principle simple: diffusion of oxygen into the metal must be prevented or slowed down. This was demonstrated by coating the active surfaces with a polymer coating.

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The spontaneous room temperature growth of low melting point metal whiskers, such as Sn, Cd, Bi, and Zn [1–6], as well as Al at elevated temperatures [7–9], is a well-established phenomenon that has resisted interpretation for over 50 years. Many models and mechanisms have been proposed: some are based on surface energy effects [10,11], stored energy [12], internal stresses [3,4], recrystallization [1], and the formation of intermetallics [6,13–18], among others [2]. Unclear to date, however, is the origin of these compressive stresses and how they result in whisker growth.

Recently, a flurry of publications [13–18] has dealt with the growth of Sn whiskers from Sn plated on Cu lead frames. In this model the origin of the macrostress is assumed to be the formation of the intermetallic, Cu_6Sn_5. This model has some deficiencies. First, the volume change for the reaction

$$6Cu + 5Sn = Cu_6Sn_5$$

is actually 5% negative and therefore more likely than not to result in tensile stresses [16]. Second, whenever residual stresses were measured in Sn thin films, they have been quite modest (≈ 10 MPa) [13–16]. Third, Sn whiskers have been observed in systems in which intermetallic formation is impossible such as the Sn-Al [1,2], or Sn deposited on glass slides [1]. Fourth, whisker activity was found to be a function of atmosphere [19,20]. Last to account for the growth of ≈ 0.3 mm Sn whiskers in a year (equivalent to a rate of ≈ 0.1 Å/s), Zheng and Tu [18] had to assume a room temperature grain boundary diffusion coefficient, D_{GB}, of Cu in Sn of the order of 10^{-8} cm^2/s. If such a D is assumed, the characteristic diffusion distance, $\sqrt{Dt}$, in a year would be around 5 mm, a value that is at least 2 orders of magnitude thicker than most thin films studied. These calculations are of fundamental importance because they unambiguously show that diffusion *alone cannot* be implicated in whisker growth for a simple geometric reason: any D_{GB} value that can account for the whisker growth rates observed would invariably wipe out any concentration gradients needed for growth.

In 1999 Ga whiskers were observed to self-extrude from Cr_2GaN bulk samples. Initially, it was postulated the basal planes of Cr_2GaN were the Ga source [21]. Shortly thereafter it was discovered that the actual Ga source was excess, or unreacted, Ga present at the grain boundaries [22]. Working with Ga was complicated by its low melting point. Recently, In (indium) structures, reminiscent of the Ga ones, were observed sprouting from predominantly single-phase samples of Zr_2InC. The main purpose of this Letter is to describe our findings and to propose a model that is consistent with our results, and many observations made over the years concerning the spontaneous growth of metal whiskers.

The Zr_2InC samples were fabricated in bulk form, by a reactive hot isostatic pressing process, the details of which can be found elsewhere [23]. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS), analyses confirmed the samples were fully dense and predominantly single phase with some unreacted In at the grain boundaries [Fig. 1(a)]. The In content, determined from differential scanning calorimetric analysis, was 4 vol. %. The majority of grains ranged in size between 3–5 μm.

After a period of several weeks at room temperature, In whiskers appeared to exude from the grain boundaries [Figs. 1(b) and 1(c)]. The striations parallel to the whisker axis [Fig. 1(b) and 1(c)] strongly suggest they were extruded. The size and shape of the whisker cross section depended on the shape of the grain boundary from which it was extruding [Fig. 1(c)]. Additionally, roughly equally spaced striations *perpendicular* to the whisker axis are observed in some micrographs [Figs. 1(c) and 1(d)]. In a few instances, a network of cracks developed during mounting of the samples. With time, these cracks filled with In, resulting in the formation of microscopic walls of In [Fig. 1(d)].

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To accelerate whisker growth, some samples were *in situ* heated in a SEM chamber and observed at a temperature below the melting temperature of In (157 °C). The whiskers (not shown) grew from their base at a rate that was constant with time. In agreement with previous work [1], there was no correlation between whisker diameters, d_w, and their growth rates, L_w. At the melting point the whiskers rapidly spheroidized and many other spheres exuded spontaneously from the surface. The sphere population then rapidly coarsened in *real time*, unambiguously proving that in this case surface energy reduction was the driving force and that the In phase was interconnected [23]. After coarsening, thin, collapsed In-oxide shells were observed on the surface indicating that some of the spheres were covered by a thin oxide layer.

To determine the effect of atmosphere on whisker growth, a sample was sectioned in two and polished with 60 nm silica particles. One sample was sealed in an evacuated glass tube; the other was left in air. After three months the glass tube was broken. SEM micrographs of the two surfaces make it clear that the surface exposed to air [Fig. 2(a)] exhibited significantly more whisker activity than the one held in vacuum [Fig. 2(b)]. Also the whiskers formed in air were significantly longer.

To confirm that the whiskers seen herein were comparable to earlier reports on Sn [24] a 50 wt. % Al-Sn alloy was melted and chill cast. After polishing, one sample was sealed in an evacuated glass tube, and another was held in air after a portion of its surface was coated with nail polish. Two weeks later, the polymer coating was dissolved in acetone and all three surfaces examined. In all cases, small Sn hillocks were observed; their densities,

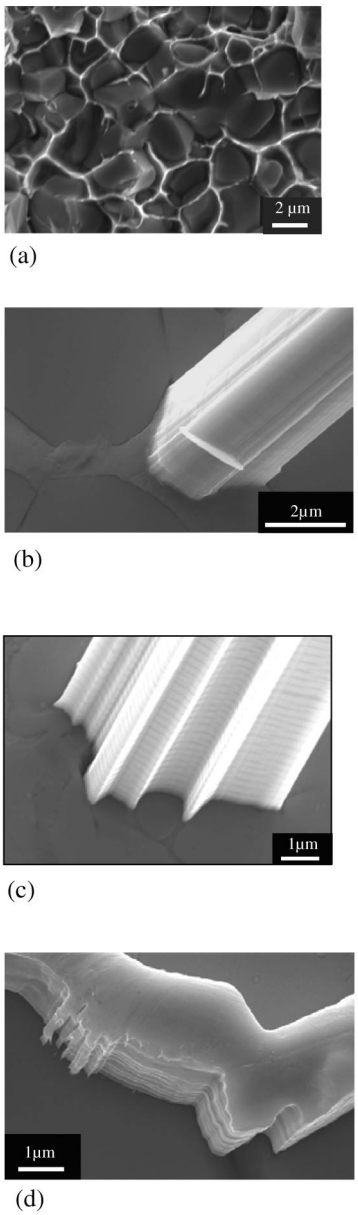

FIG. 1. SEM micrographs: (a) fractured Zr_2InC surface showing In at grain boundaries (this surface is covered with a thin In film); (b) whisker growing from the grain boundaries of Zr_2InC; (c) another whisker whose the cross-sectional shape is determined by grain boundary geometry at the In/Zr_2InC interface; (d) an In "wall" growing out of a crack. In both (b) and (c), note striations parallel to the whisker axis. In (c) and (d) note nearly equally spaced striations parallel to the sample surface.

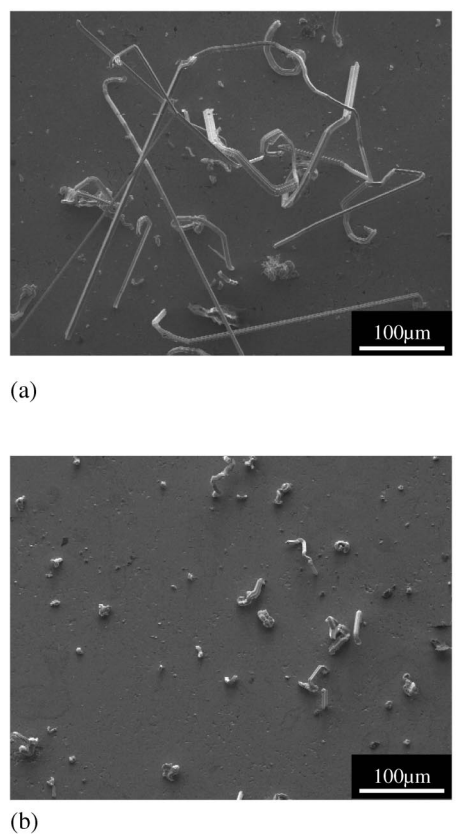

FIG. 2. Whisker activity after three months of two halves of a Zr_2InC sample, in which one-half was held in (a) air, and the other half in (b) an evacuated glass tube.

however, were higher in the surface exposed to air. More importantly, whiskers sprouted exclusively from the air-exposed surfaces.

These results are crucial because they imply the driving force for whisker growth is a reaction between oxygen, O, or nitrogen, N, and the soft metal (SM) In or Sn. Since N was not found in the whiskers, but O was [23], and O is more reactive, we assume O to be the culprit. The simplest reaction is the dissolution of O in the SM, with the volume change, ΔV, providing the driving force. However, the very low room temperature O solubilities in the SMs preclude this from being the major driving force.

The more likely scenario is the one shown schematically in Fig. 3(a). The O is assumed to diffuse down the SM/substrate interfaces and form a SM oxide. The stress fields that result from the relative volume change, $\Delta V/V_0$, associated with the latter were estimated using a finite element code. Here we modeled the Al-Sn microstructure (not shown) in which the Al matrix grains were presumed to be cylinders $\sim$40 μm in diameter; the minimum width of the Sn was $\approx$ 5 μm [Fig. 3(c)]. Initially the arrangement is considered to be stress free; ΔV is simulated by allowing the oxide layer to expand by 25% [25]. The out-of-plane stress, σ_{33}, that will tend to push the Sn whiskers outward, presumably through a thin native surface oxide layer (not shown), is compressive [Fig. 3(b)]. Assuming a SnO_2 thickness, δ, of 100 Å, σ_{33} is $\approx$ 50 MPa. This value is conservative in that it assumes a δ of 100 Å. Clearly, larger values of the ratio of δ to grain size and higher volume fractions, v_f, of Al would lead to even higher values of σ_{33}. For example, for 4 μm grains (i.e., a microstructure closer to the one shown in Fig. 1), σ_{33} can reach 200 MPa. Although the exact level of σ_{33} that develops in a real microstructure may be different due to the 2D character of the simulation and the idealization of the

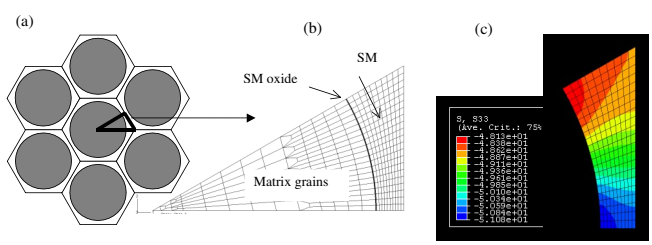

FIG. 3 (color online). (a) Periodic hexagonal arrangement of Al grains (gray) surrounded by a thin oxide layer (not shown) and Sn (white). (b) Plane strain finite element mesh for the analysis of the effect of oxide expansion: Al grain size, 40 μm; minimum width of Sn layer, 5 μm; oxide thickness, 100 Å; volume fraction v_f of Al, 71.7%; actual v_f = 73%. Because of symmetry, it was sufficient to model a 30° slice subject to constrained periodic boundary conditions. (c) Contours of out-of-plane stress in Sn in MPa. The material properties chosen are Young's modulus of Al, $E_{Al} = 70$ GPa, Poisson's ratio, $\nu_{Al} = 0.3$; of Sn, $E_{Sn} = 50_{Sn}$ GPa, $\nu_{Sn} = 0.37$; and of SnO_2, $E_{SnO} = 263$ GPa, $\nu_{SnO} = 0.29$.

boundary conditions applied here, the model shows that ΔV can provide an appropriate driving force for whisker extrusion.

One advantage of our model is that it does *not* imply diffusion is rate limiting; the ingress of O and associated ΔV can occur at a much different time scale than that for the extrusion of the whiskers. A useful analogy is a bicycle tire that is pumped and slowly leaks through a fine hole over a much longer time. Consequently, linear growth rates, L_w, are possible. Another important test of any model proposed is whether it can account for some of the faster rates values of L_w reported. Assuming the rate of O diffusion into the grain boundary, L_{GB}, is linear (a good assumption at least initially), a simple mass balance yields

$$\frac{L_w}{L_{GB}} = \frac{4\delta d_M n}{d_w^2}\left(\frac{\Delta V}{V_0}\right), \tag{1}$$

where δ is the thickness of the SM that is converted to oxide, n is the number of grains contributing to the growth of a whisker, and d_w and d_M are the whisker and matrix diameters, respectively. Making some reasonable assumptions [26], it can be shown that the left-hand side of Eq. (1) equals 10, if 100 grains contribute to the growth of one whisker. In other words, the ΔV due the diffusion of O into *numerous* near-surface interfaces translates into the extrusion of long whiskers from specific surface sites.

In the remainder of this Letter evidence from this and previous work for the model proposed is presented. First, the key role O (or N) plays in the process is explained. Our model is also consistent with the fact that atmospheric O_2 and water vapor accelerate whisker growth [20]. Similarly, it explains why Cd thin films, held in vacuum for up to 34 days, grew no whiskers, but, when the same films were exposed to air, short (5 to 10 μm long) whiskers appeared after only 3 days [19].

Our model requires the presence of O and it was thus somewhat surprising to detect hillock and incipient whisker formation in evacuated environments such as the SEM or the sealed tubes [Fig. 2(b)]. We attribute this activity to the presence of trace amounts of O in the atmospheres, or, more likely, to O adsorbed on the sample surfaces prior to their sealing. It is not unreasonable to assume such adsorbed gases can first diffuse along the surface prior to diffusing down the relevant interface temporarily fueling growth. This hypothesis is consistent with the fact that the whiskers grown in vacuum are shorter (Fig. 2). Such a scenario also explains why, when Al thin films were deposited and/or annealed in ultrahigh vacuum (UHV), no hillock formation occurred [7]. When similar films were deposited in HV (where the O activity was higher), annealed in HV, or exposed to air and then annealed in UHV, hillocks formed. In other words, hillock growth was correlated to the exposure of the Al films to air and/or residual O.

Second, as discussed above, our model can account for the linear growth rates observed over periods as long as 360 days [1,24]; a crucial result *impossible* to explain by diffusion alone [6,13–18]. As long as the right-hand side of Eq. (1) is >1, the pressure will build up in the SM. Also note that as n increases, as occurred in one sample where there was only one active site [22], the growth rate can be phenomenal—0.5 m in $\approx$ 1 yr.

It is not claimed here that reaction with the atmosphere is the only reason for the growth of SM whiskers. It is well established that external compressive stresses can enhance whisker growth rates by factors as high as 10 000 [3–5,9,27].

The main and critical prediction of our model is that continued whisker growth can be prevented by the provision of an oxygen diffusion barrier layer. This was confirmed by the nail polish experiment. Additionally, when the Zr_2InC samples were heated in air to modest temperatures their ability to exude In was destroyed, presumably due to the formation of a relatively thick oxide layer through which the whiskers could not penetrate and/or O diffusion down the relevant interfaces was slowed down. The same was observed for Sn thin films oxidized at 200 °C [20]. Furthermore, freshly fractured surfaces appear to be more active than polished surfaces. A good example is the filling of cracks formed during mounting of the sample with In [Fig. 1(d)]. In general most thin cracks get filled with In, in contradistinction, only select areas on the surface exude In. The filling of these cracks is presumably a two-step process: first, the grain boundaries exposed to the fresh surfaces exude In into the crack and fill it up. Then, once filled, the process continues by the mechanism proposed in Fig. 3. In agreement with our model, fractured surfaces that exposed thin films of In were inactive, presumably because the oxidation of such surface films *cannot* generate the stresses needed for whisker growth. In a crack, the volume expansion is constrained.

In summary, we propose a plausible, oxidation-based process for the growth of metal whiskers that goes a long way in solving a 50+ year old problem. This comment notwithstanding, it is hereby acknowledged that several questions remain unresolved. One is why whiskers much smaller than 1 μm in diameter are not typically observed. Our model can account for why structures with diameters or thicknesses much greater than, say, 10 μm are not observed (the stresses generated would simply be too small to extrude the fibers), but not why thinner ones do not. That said, as the fiber diameter shrinks, the frictional forces required to extrude it will rise rapidly, which could explain the absence of smaller diameter fibers. Another question is why whisker growth is apparently a thin film phenomenon in Sn [1]. Nevertheless, the solution to this pesky problem is in principle simple: oxygen should be prevented from accessing any potentially active surface. Last, a better understanding of this process and how to control it could lead to the *in situ* fabrication of complex structures involving micro- or nanowires [27].

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