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A molecular dynamics evaluation of the effect of dopant addition on grain boundary diffusion in tin: Implication for whisker growth

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ABSTRACT

Addition of lead dopant has been known to be an effective way of mitigating whisker growth in tin. However, the toxic nature of lead has necessitated a search for alternative dopant species. Recent investigations have indicated that indium can be an effective agent in reducing whisker growth. In an effort to investigate if reduction in diffusivity of tin atoms near grain boundaries in presence of dopant atoms is the underlying mechanism that causes reduced whisker growth, we employed molecular dynamics simulations to model tin grain boundaries with lead and indium dopants. We simulated pure tin grain boundary as well as grain boundaries with 4% dopants by mole fraction. Our results indicate that the dopant atoms segregate near the grain boundary and forms clusters, which in turn leads to reduced diffusivity of tin atoms by up to a factor of three. Since such reduction in diffusivity alone cannot reduce whisker growth by several orders of magnitude, we conclude that other mechanisms might play a more dominant role in mitigating tin whisker growth.

1. Introduction

In electronic packages, copper lead-frames are often electroplated with 5–20 μm thick tin (Sn) or a Sn-rich alloy to reduce oxidation and serve as a wetting-enhancer during subsequent soldering for lead (Pb) attachment. Frequently, Sn whiskers, which may be hundreds of micrometers long, extrude from the electroplated surface during storage, causing electrical shorts between neighboring circuitry [1–3]. Whiskers have been observed in various systems (including Sn on Cu, Zn on steel and Al on Si) since the 1950s [3–22]. A number of reasons for whisker formation have been suggested, but there is now a consensus that 3 key conditions have to be satisfied for whiskers growth [5,12,13,18,19,23,24]. These are: (1) a mechanism to continually generate in-plane compressive stresses within the coating to provide the driving force for whisker growth, such as continuous formation of an interfacial reaction product (e.g., Cu_6Sn_5 for Sn coatings on Cu), (2) a tenacious surface oxide layer which limits surface vacancy sources, thereby precluding stress-relief via diffusional processes, and (3) rapid grain boundary self-diffusion of Sn to transport matter from the plating-interior to the growing whisker. Indeed, the presence of vertical columnar grain boundaries has been suggested to provide a rapid path for feeding whiskers [20], although by itself, this mechanism is not consistent with the continuing presence of in-plane compressive stress.

It has been known since the 1960s that the addition of 1–3% of Pb to the Sn plating leads to complete mitigation of whiskering [5], and until recently, doping with Pb has been the primary approach for whisker mitigation in Sn. However, the recent regulatory ban on Pb in electronics has led to the urgency in developing alternative approaches for Sn whisker mitigation. These have comprised including some porosity in Sn platings [14], depositing a Ni inter-layer between the Cu substrate and Sn, and the use of conformal over-coats on Sn [23,24]. However, none of these approaches has proved to be as effective or versatile in reducing whisker growth as doping with Pb.

Recently, the addition of 5–10% indium (In) has been shown to completely prevent the growth of long whiskers (aspect ratio >5) from electroplated Sn coatings [25,26] in samples aged at room temperature up to 1000 h, proffering In dopants as a suitable alternative to Pb. In this work, In was chosen as a dopant primarily because: (a) its atomic number is close to that of Sn (49 for In, 50 for Sn), minimizing the likelihood of chemical interaction; (b) In has moderate solubility in Sn (around 4 wt% at room temperature), which reduces the chance of precipitation of In within the Sn grains, and (c) like Pb, its atomic radius is larger than that of Sn (1.67 Å for In vs. 1.51 Å for Sn), potentially facilitating the segregation of In atoms near Sn grain boundaries, and thereby slowing grain boundary self-diffusion of Sn to feed whisker growth. Although the need for a stress gradient as the driving force for

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Table 1
Effect of solute atoms on GB diffusivity/activation energy for diffusion.

Solvent	*Solute*	*at % solute*	*Grain boundary diffusivity of solvent atoms*	*Ref*
Fe	S	3.5×10^{-7}	Q_{gb} (pure Fe)=99 kJ/mol Q_{gb} (Fe/S)=164 kJ/mol	[41]
Fe	Sn	0.25	δD_{gb} (pure Fe)=4×10^{-21} m^3/s at 681 °C δD_{gb} (Fe/Sn)=2×10^{-21} m^3/s at 681 °C	[31]
Fe	Sb	0.03	δD_{gb} (pure Fe)=4.8×10^{-22} m^3/s at 550 °C δD_{gb} (Fe/Sb)=8×10^{-21} m^3/s at 550 °C	[42]
Fe	Sb-Ni	Sb=0.03 Ni = 1.0	δD_{gb} (pure Fe)=5×10^{-22} m^3/s at 550 °C δD_{gb} (Fe-Sb/Ni)=1.4×10^{-21} m^3/s at 550 °C	[42]
Cu	S	5×10^{-7} vs. 1.5×10^{-6}	δD_{gb} (Cu-5×10^{-7} of S)=2.1×10^{-21} m^3/s at 445 °C δD_{gb} (Cu-1.5×10^{-6} of S)=8.1×10^{-22} m^3/s at 445 °C	[28]
Cu	Ag	0.091	Q_{gb} (pure Cu)=90 kJ/mol Q_{gb} (Cu/Ag)=119 kJ/mol	[43]
Au	Ta	1.2	Q_{gb} (pure Au)=84.9 kJ/mol, Q_{gb} (Au/Ta)=121.6 kJ/mol	[44]

Sn-whisker growth has been widely studied [12,19,21], and Cu-Sn intermetallic formation is well-known as the mechanism for continuously regenerating the stress to compensate for diffusionally driven relaxation [16], the root reason why alloy addition may alter the stress-state or whisker growth is unclear. Indeed, despite the clear evidence that Pb dramatically reduces whisker growth, as does In, there has been no reported study on the role of these alloy additions on Sn self-diffusion along the grain boundaries. This is particularly surprising, since transmission electron microscopy clearly shows segregation of Pb precipitates at Sn grain boundaries even with only 2 wt% Pb [12].

It was therefore deemed necessary to evaluate the possible role of dopant atoms, such as Pb and In, on the grain boundary diffusivity of Sn atoms, and therefore on their potential influence on whisker growth rate in Sn coatings. The interatomic interactions leading to localized segregation and any interference with the diffusing species occur at extremely small length and time scales and, therefore, cannot be directly accessed by continuum models. For instance, the ability of Sn atoms to segregate from the bulk and diffuse to the interface depends primarily on the interactions between the atoms constituting the interface and the dopant atoms. Therefore, the purpose of this study is to use a molecular dynamics (MD) approach to: (1) validate the tendency for Pb atoms to segregate at Sn grain boundaries, (2) examine whether similar interactions occur between In atoms and Sn grain boundaries, and (3) evaluate the effect of Pb and In solute atoms on grain boundary self-diffusivity of Sn. The objective is to assess whether boundary self-diffusivity can be sufficiently slowed by dopant segregation to explain the dramatic reduction in Sn whisker growth seen as a result of the additions of Pb and In.

2. Background

2.1. Influence of solute atoms on grain boundary self-diffusivity

Often, the incorporation of solute atoms, and segregation thereof at grain boundaries, reduces grain boundary self-diffusivity in alloys. Segregation of solute atoms at the grain boundary occurs even at very small solute concentrations (i.e., $\alpha = C_{gb}/C_v > 1$, where C_{gb} is the grain boundary concentration, and C_v is the concentration within the volume or grain interior) [27,28]. Some solute atoms segregate severely ($\alpha >> 1$) whereas some solute atoms for a given solvent metal segregate only weakly ($\alpha > 1$ but $\alpha < 10$). The extent of the segregation depends on the rate at which grain boundary energy increases per solute atom, as per the Gibbs adsorption equation [29,30]. Empirical evidence suggests that the extent of segregation would be severe if the solute solubility limit is small [30], and is greater at high-angle grain boundaries [29,30]. Furthermore, it is also observed that the segregation of substitutional solute atoms at grain boundaries increases activation energy and reduce grain boundary diffusivity in many metals [27,29,31]. This is also true for ceramics, where misfit strain associated with a large dopant ion significantly reduces grain boundary diffusion and can result in drastic reduction of creep rate [32–34].

2.2. Previous MD work, Sn grain boundary misorientations

MD simulations [35–37] present fundamental theoretical techniques that can account for atomistic interactions and can hence accurately model diffusion at metallic surfaces [38] and interfaces [39–41]. Recently, MD simulations were conducted on self-diffusivity in various tilt boundaries as well as solute segregation on β-Sn grain boundary [39,40]. These studies report that the highest energy boundaries are associated with largest boundary width. In general, the boundary width decreased with addition of solute to Sn, depending on the relative magnitudes of the solute-Sn and Sn-Sn cohesive energies. Although some of this work considered highly non-equilibrium amounts of small solute atoms in interstitial positions [40], generally, segregation of solute at GB appears to reduce GB self-diffusivity significantly [22]. For instance, in a separate MD study, it was shown that atoms either smaller or larger than the solvent reduced GB energy, with the effect being largest for larger atoms [42]. Table 1 shows a summary of the effect of solute atoms on width-scaled grain boundary diffusivity ($\delta_{gb}D_{gb}$) or the activation energy for grain boundary diffusion (Q_{gb}) [28,31,43–46]. In the majority of cases, Q_{gb} increases significantly upon solute addition, whereas $\delta_{gb}D_{gb}$ decreases.

However, the literature lacks a systematic and detailed computational study that addresses the role of additives on the diffusion of Sn in the vicinity of realistic grain boundaries. In the present study, classical MD simulations were conducted to directly account for interaction of Pb and In dopant atoms with Sn and determine their role on the diffusion of Sn atoms at grain boundaries. Pb is widely known as a dopant atom that slows down the growth of Sn whiskers and was therefore selected as a model dopant in the present study. As an alternative to generate Pb-free devices, In has been recently explored and shown to mitigate whisker growth. Therefore, the present study also investigated In as a dopant species.

3. Methodology

The Sn grain boundary was constructed based on an interface bounded by two single crystals of Sn. As a first step, the unit cell of