Grain boundary segregation: equilibrium and non-equilibrium conditions

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Abstract

The segregation of Bi to Cu grain boundaries can be characterized as either equilibrium or non-equilibrium segregation. The experimental conditions of the segregation process determine the type of segregation behavior that is achieved. Classical McLean equilibrium segregation can be achieved through Bi grain boundary segregation from a constant vapor source with long anneal times. The Chang dislocation-pipe diffusion model of Bi segregation more accurately describes the onset of Bi segregation from an instantaneous source for short anneal times. A discussion on the conditions defining Bi segregation behavior is presented.

Keywords: Grain boundary; Segregation; Kinetics; Copper; Bismuth

1. Introduction

For over 100 years, the grain boundary segregation of Bi into Cu has been known to occur and is well-documented [1]. The Cu–Bi phase diagram indicates that the maximum solubility of Bi in the Cu lattice is on the order of 200 at. ppm [2]. The extremely low solubility of Bi in the Cu lattice and the affinity of Bi for the Cu grain boundaries makes this an attractive system for investigating basic segregation behavior in grain boundaries. For example, Bi segregation studies have been performed in order to understand the embrittlement phenomenon in Cu grain boundaries and to study the general segregation behavior of Bi in Cu [1,3–11].

It is noted in this paper that the material processing methods that have been used to achieve the segregation of Bi to Cu grain boundaries may be separated into two general techniques. The first technique shall be referred to as the vapor exchange (VE) technique and the second technique shall be referred to as the dope-segregation (DS) technique. Both of the techniques have been carried out in a vacuum encapsulated silica tube, under slightly different experimental conditions. In the VE technique, the Cu sample is exposed to a Bi vapor source at a single temperature for the segregation process. In the DS technique, the Cu...
sample is doped with Bi, either from the melt or from a diffusion doping process at a higher temperature than the final segregation temperature. Then in a second annealing step, typically at a lower temperature, the segregation occurs at the final segregation temperature. Thus, the most important distinction between the two is that in the VE technique an external Bi vapor source is provided during the segregation anneal, while an external Bi vapor source is not present during the segregation annealing process using the DS technique. As will be described below, a difference in the experimental procedures used for the segregation process will produce very different types of segregation behavior. These different behaviors are attributed to the fact that some of the anneals are conducted at equilibrium conditions and some are not conducted at equilibrium conditions.

2. Discussion

In several instances, the term “equilibrium” has been loosely applied to describe the overall segregation behavior of Bi in Cu without due consideration given to the thermodynamics and kinetics of the experimental segregation process [1,3–6]. As explained below, the use of the term “equilibrium segregation” may not be accurate in all cases in the literature. Thus, the segregation of Bi to Cu grain boundaries may be defined as either equilibrium or non-equilibrium segregation, depending upon the thermodynamics and the resulting kinetics of the material processing methods. It is suggested that the distinction of “equilibrium grain boundary segregation” be used only when true equilibrium conditions are present.

The report by Michael and Williams [4] most closely resembles that of the VE method (they actually used a two step annealing process). Michael and Williams indicated that Cu segregated for 12 days correlated well with theoretical calculations using the McLean model. The data from Michael and Williams provides the best evidence that the VE technique allows for McLean type kinetics and equilibrium segregation.

The report by Chang et al. [5] most closely resembles the DS method. In an investigation of the kinetic aspects of Bi segregation, Chang et al. [5] used the DS technique in order to achieve Bi segregation. Polycrystalline Cu samples were doped from the melt and homogenized at 1000 °C prior to the segregation anneals at 600 °C for various times. According to Chang et al. [5], the McLean type segregation model tends to overestimate the time needed for segregation by several orders of magnitude. However, the apparent overestimation of the time needed for segregation may be attributed to the experimental conditions used as shown below.

While the McLean model is based on the assumption that the Bi is transported to the grain boundary via a volume diffusion mechanism using the VE technique, Chang et al. [5] have shown experimentally and through modeling that the method of Bi transport that leads to an experimental maximum grain boundary concentration is via a dislocation-pipe diffusion mechanism using the DS technique. Thus, the very nature of the experimental conditions has dramatic influence on the segregation kinetics. Equilibrium segregation is known as Gibbsian segregation. Equilibrium segregation has been related to McLean-type surface adsorption isotherms [12]. The McLean model as applied by Chang et al. [5] to the grain boundary segregation of Bi to Cu is shown in Eq. (1).

\[ \frac{c^b(t) - c^b(0)}{c^b(\infty) - c^b(0)} = 1 - \exp \left( \frac{4Dt}{s^2\delta^2} \right) \text{erfc} \left( \frac{2\sqrt{Dt}}{s\delta} \right) \]

(1)

In Eq. (1), \( c^b(0), c^b(t) \) and \( c^b(\infty) \) are the initial, the time dependent and the equilibrium concentration of Bi in the grain boundary, respectively. The volume diffusion coefficient of Bi in Cu is \( D \), \( t \) is the segregation time, and \( \delta \) is the grain boundary width. The Bi segregation factor \( s \) is equal to \( c^b(\infty)/c^b \), where \( c^b \) is the initial bulk concentration of the Bi in the Cu. The time necessary to achieve 90% saturation time, \( t_{0.9} \), for the McLean model is shown in Eq. (2).

\[ t_{0.9} = \frac{7.5s^2\delta^2}{D} \]

(2)

Within the last few years Chang et al. [2,5,9,10] have performed extensive work on the Cu–Bi system. Chang et al. [5] have experimentally developed the Cu–Bi phase diagram in the ppm-Bi
region and have proposed a new type of segregation model for the Cu–Bi system based on their DS experiments. The new type of segregation behavior is based on a dislocation-pipe diffusion model shown in Eq. (3).

$$c^\Phi(t) - c^\Phi(0) = \frac{L \rho^d c^b D t}{2\delta} \quad t < t_{sat};$$
$$c^\Phi(t) = c^\Phi(\infty) \quad t \geq t_{sat}$$  (3)

In Eq. (3), the value $L$ is an effective length related to the grain size and $\rho^d$ is the dislocation density. Chang et al. [5] studied the kinetic aspects of Bi segregation in Cu and determined that the time necessary to saturate a grain boundary, $t_{sat}$, is in accordance with Eq. (4), which is derived from the use of a dislocation-pipe diffusion model.

$$t_{sat} = \frac{2\pi\delta}{L\rho^d D}$$  (4)

Comparing Eqs. (2) and (4) it is noted that the value of $t_{sat}$ is several orders of magnitude smaller than the equivalent McLean 90% saturation time $t_{0.9}$. Thus, by comparing the two data sets obtained under different conditions (i.e. from Michael and Williams, and Chang et al.) it can be inferred that a difference in the experimental parameters has a profound influence on the segregation kinetics.

A comparison of the two models for saturation time is shown in Fig. 1, where the Bi concentration in monolayers (MLs, 1 ML = 9.3 atoms/nm$^2$) [5] is plotted as a function of time. The data points in Fig. 1 are from a Bi segregation experiment performed by Chang et al. [5] in which a polycrystalline Cu sample containing 50 at. ppm Bi was annealed at 600 °C for various times in order to attain what they refer to as grain boundary saturation. Chang et al. used the following values: the diffusivity, $D$, is calculated using $D_0 = 7.66 \times 10^{-5}$ m$^2$/s and $Q = 178.1$ kJ/mol, the grain boundary width, $\delta$, is assumed to be 1 nm, the effective length, $L$, is 500 µm, the dislocation density, $\rho^d$, is $10^{11}$ m$^{-2}$, the segregation factor, $s$, is $5 \times 10^4$ [13], and the bulk concentration, $c^b$, is 50 at. ppm. As shown in Fig. 1, the Bi concentration should increase rapidly for the Chang model until it reaches a maximum value. Whereas in the McLean model, a maximum value is presumed to be obtained very slowly. (Note that Chang assumes that the maximum concentration value is the same in both models.)

The Chang dislocation-pipe diffusion model fits the data obtained from the DS technique very well until $\approx 10^5$ s. Chang et al. [5] did not explain the reason for the consistent decrease in the Bi concentration that occurred in most of their experiments for the segregation anneals longer than $\approx 10^5$ s. Chang et al. [5] indicated that the Bi segregation reached “equilibrium saturation”. However, this should more appropriately be referred to as just a maximum concentration value since the Bi segregation concentration decreases with time after saturation is reached.

The discrepancy between the McLean model and the Chang [5] models for Bi segregation can be readily explained. Using the DS process, the Cu is first doped to the desired concentration utilizing an external Bi vapor source, and then segregated without the presence of an external Bi vapor source in an evacuated tube at a lower temperature. Given enough time, the Bi will saturate the Cu grain boundary (i.e., the Bi concentration will reach a maximum value). However, without the presence of an equilibrium partial pressure of Bi present during annealing, the Bi concentration along the grain boundary will deplete with time as the Bi escapes from the grain boundary into the vapor phase until an equilibrium partial pressure is reached. The result is a slow decrease in the grain boundary segregation level over time after a sharp maximum value is achieved. The data from Chang et al. [5,10] show the reduced segregation levels for long anneal times as is shown in Fig. 1.
Fraczkiewicz and Biscondi [11] also provide evidence of the time dependent Bi segregation levels. In addition, the inclusion of the work by Alber et al. [6] lends credibility to the time dependence of the Bi segregation phenomenon. Alber et al. [6] used the DS procedure for Bi segregating Cu bicrystals, with very long segregation times (i.e., from two days at 950 °C up to four weeks at 600 °C). The lower Bi segregation levels recorded from Alber et al. [6] are quite possibly due to the longer annealing times.

It has been shown that both the kinetics and the Bi segregation levels vary significantly between the VE process and the DS process. In the VE method, segregation of the Bi to the Cu grain boundaries occurs via a constant source from the vapor phase in contrast to the DS method where the diffusion mechanism is based on an instantaneous source from within the crystal. Using the VE technique, grain boundary saturation is achieved very slowly under equilibrium conditions. For the anneal times used in the Chang experiments, the DS technique for segregation kinetics results in a time dependent increase, and then decrease, of the Bi concentration at the grain boundary, without achieving equilibrium conditions. Thus, true equilibrium segregation occurs when a constant Bi vapor source is provided as in the VE method and/or by using the DS method only if a sufficiently long anneal time is allowed. It should be emphasized that caution must be observed when using the term equilibrium. The term equilibrium is simply a homeostatic state that exists between the pressure, temperature and volume of a given system. Since the pressure is a function of the number of moles of Bi available, the values for the grain boundary concentration and/or the Bi vapor pressure will not necessarily be equal between the two methods even if both systems are at their respective equilibrium states for a given temperature. Recalling that the source in the DS method is instantaneous (i.e., a finite quantity of Bi is contained in the bulk), equilibrium conditions for that system may be significantly different than the equilibrium conditions for the VE system characterized by a constant diffusion source provided by an external Bi vapor phase. If a hybrid method is used where a Bi vapor source is used during the DS type segregation anneal, equilibrium may be reached according to the McLean model. Thus, it is believed that the Chang model for segregation kinetics will more accurately reflect equilibrium conditions when the DS technique is used in conjunction with the presence of an additional source of Bi vapor during the segregation anneal. Therefore, three scenarios are possible for segregation behavior using different variations of the DS technique. Fig. 2 shows a schematic diagram of the three possible scenarios for the case where (1) an external Bi vapor source is present, (2) no external Bi vapor source is present and an equilibrium vapor pressure is achieved at some point during the segregation anneal, and (3) no external Bi vapor source is present and equilibrium vapor pressure is not achieved during the segregation anneal.

In scenarios 1–3, a grain boundary reaches a maximum Bi concentration according to the Chang model (the actual maximum value and the time to reach this value is dependent upon grain boundary structure and other experimental conditions related to the anneals). After a maximum value is reached, three scenarios are possible. In scenario 1, the maximum Bi concentration is maintained due to the use of an external vapor source that provides an equilibrium Bi vapor pressure which prevents depletion of the Bi from the grain boundary into the vapor phase. In scenario 2, since there is no external Bi vapor source, the Bi is depleted from the grain boundary until an equilibrium Bi vapor pressure is established. Thus for scenario 2, the segregation kinetics and the Bi concentration in the grain boundary are a function not only of

![Fig. 2. A schematic drawing of the Bi segregation behavior scenarios using variations of the DS technique.](image)
the diffusivity, but also of the time needed to establish the equilibrium Bi vapor pressure. In scenario 3, there is no external Bi vapor source and an equilibrium Bi vapor pressure is never achieved. Thus, the Bi continues to deplete from the grain boundary over time. Note that the time where the maximum segregation value begins to decrease need not be the same for scenarios 2 and 3. In summary, for the experiments depicted in scenarios 1 and 2, equilibrium segregation conditions are achieved at some point during the experiment. However, within the time frame shown for scenario 3, equilibrium segregation is never reached.

3. Conclusions

The exact nature of the Bi segregation behavior in Cu is strongly dependent on the experimental parameters used during the segregation process. There are two widely used models that describe grain boundary segregation kinetics. The McLean model fits well to Bi grain boundary segregation from a constant vapor source. The Chang model accurately describes the onset of Bi grain boundary segregation originating from an instantaneous source within the bulk. It is believed that the Chang model would accurately depict equilibrium segregation with the DS technique if a Bi vapor source was also present. It has been clearly shown that there is a distinct difference between equilibrium segregation and non-equilibrium segregation. Great care should be exercised to use these terms appropriately when modeling the type of kinetics that is used in the segregation process.

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References