

Segregation measurements of In and S on a Cu(In,S) ternary alloy using Auger Electron Spectroscopy coupled with a linear programmed heater

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Abstract. In this study a dilute Cu(In,S) ternary alloy was prepared by a diffusion doping process. From a prepared Cu(In,S) ternary alloy, the segregation behaviour of In and S was measured using Auger Electron Spectroscopy (AES) coupled with a linear programmed heater. From the measured segregation profiles it was found that the In segregated first followed by S. The S completely replaced the In from the surface indicating that S has a larger segregation energy than In. From the segregation profiles the segregation parameters, namely the pre-exponential factors (D_0), the activation energies (Q), the interaction energies (Ω) and the segregation energies (ΔG) were extracted with the modified Darken model for In ($D_0 = (2.2 \pm 0.5) \times 10^{-5} \text{ m}^2/\text{s}$, $Q = 184.3 \pm 1.0 \text{ kJ/mol}$, $\Delta G = -62.8 \pm 1.4 \text{ kJ/mol}$, $\Omega_{\text{Cu-In}} = 3.0 \pm 0.4 \text{ kJ/mol}$), S ($D_0 = (8.8 \pm 0.5) \times 10^{-3} \text{ m}^2/\text{s}$, $Q = 213.0 \pm 3.0 \text{ kJ/mol}$, $\Delta G = -120.0 \pm 3.5 \text{ kJ/mol}$, $\Omega_{\text{Cu-S}} = 23.0 \pm 2.0 \text{ kJ/mol}$) and the atomic interaction ($\Omega_{\text{In-S}} = -4.0 \pm 0.5 \text{ kJ/mol}$) for In and S.

1. Introduction

It is a general observation that certain elements (impurities) in a dilute homogeneous alloy, accumulate at the grain boundaries and free surfaces of a material as a result of a segregation process [1]. The grain boundaries are responsible for the strength and hardness of a material [2]. The free surface of a material is a very active region for processes such as catalytic reactions, epitaxial growth of thin films, corrosion, thermionic emission, etc. Therefore, the segregation of impurities to the grain boundaries of a material influences the metal-metal bonding at the grain boundaries and as a result the strength and hardness of a material can be influenced, the segregation at the free surface can influence processes mentioned above that take place at the free surface of the material. Consequently, segregation of impurities at the grain boundaries and free surfaces of a material play a vital role in engineering of materials.

There is a considerable number of segregation studies on the segregation of impurities (Bi, Sb, Sn, S, Ag, etc.) from Cu [3–7]. Despite the considerable number of publications concerning segregation of impurities from a Cu crystal, no study was found for In segregating from a Cu crystal. Therefore, this study is most likely the first to report on the segregation of In from a Cu crystal. Note that S is a regular impurity in a Cu crystal (with bulk concentration in the order of few parts per million (ppm)) and is anticipated to segregate with In to give a Cu(In,S) ternary alloy.

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This study focuses mainly on the segregation of In from a Cu crystal. The segregation of S from a Cu crystal will also receive attention. Nevertheless, the segregation of S from a Cu crystal was experimentally observed by Viljoen et al. [4] and in this observation only the pre-exponential factor (D_0) and the activation energy (Q) were reported. The segregation of In and S will be measured from a prepared Cu(In,S) alloy with Auger electron spectroscopy (AES) coupled with a linear programmed heater. From the measured segregation profiles a set of segregation parameters, namely the pre-exponential factor (D_0), activation energy (Q), segregation energy (ΔG) and interaction energy (Ω) will be extracted for both In and S segregation from a Cu crystal using the modified Darken model. The initial parameters of the Darken calculations will be extracted from the fits done with the Fick's and Guttman model.

2. Theory

In segregation studies the primary mechanism of surface enrichment is the diffusion from the bulk, hence it is possible to determine the bulk diffusion parameters (D_0 and Q) of the segregating impurities. Theoretically, the best known model in this regard is the modified semi-infinite model of Fick [4,8]. In this model the surface enrichment factor (β) at temperature, T , is given by $\beta(T) = (X^\phi(T) - X^B) / X^B$ where $X^\phi(T)$ is the surface concentration at temperature, T , and X^B is the bulk concentration of the segregating impurity. The temperature dependence of the enrichment factor is given by

$$\beta^2(T) = \gamma \int_{T_0}^{T_f} e^{-Q/RT} dT \quad (1)$$

where $\gamma = 4D_0 / \pi \alpha d^2$, D_0 is the pre-exponential factor, α is the constant heating rate, d is the thickness of the segregated layer, T_0 is the initial crystal temperature, T_f is the final crystal temperature, Q is the activation energy and R is the gas constant.

The modified semi-infinite model of Fick is adopted for describing the kinetic region of the segregation profiles and for extracting the D_0 and Q values from a single segregation run. During the segregation process, the concentration of the segregating impurities change between the bulk layers, B , and the surface layer, ϕ , while increasing to higher concentrations in the surface layer of the crystal until the total energy of the crystal is lowest (the equilibrium is reached). The model that is well known to describe the equilibrium region of the segregation profiles in multicomponent segregation is the Guttman model given by [9]

$$X_1^\phi = \frac{X_1^B e^{(\Delta G_1/RT)}}{1 - X_1^B + X_1^B e^{(\Delta G_1/RT)} - X_2^B + X_2^B e^{(\Delta G_2/RT)}} \quad (2)$$

$$X_2^\phi = \frac{X_2^B e^{(\Delta G_2/RT)}}{1 - X_2^B + X_2^B e^{(\Delta G_2/RT)} - X_1^B + X_1^B e^{(\Delta G_1/RT)}} \quad (3)$$

where $\Delta G_1 = \Delta G_1^0 + 2\Omega_{13}(X_1^B - X_1^\phi) + \Omega'(X_2^\phi - X_2^B)$, $\Delta G_2 = \Delta G_2^0 + 2\Omega_{23}(X_2^B - X_2^\phi) + \Omega'(X_1^\phi - X_1^B)$,

$\Omega' = \Omega_{12} - \Omega_{13} - \Omega_{23}$, ΔG_i is the segregation energy for a segregating impurity i and Ω_{ij} is the interaction energy between the atoms of the impurity i and the crystal j .

Therefore, the Guttman model yields the segregation ΔG and the interaction Ω energies. The modified semi-infinite model of Fick and the Guttman model describe the kinetic and the equilibrium regions of the segregation profiles respectively and independently. Nonetheless, the model that describes the kinetic and the equilibrium regions at once is known as the modified Darken model [9].

In the modified Darken model the crystal is divided into $N + 1$ layers of thickness d , parallel to the surface. According to this model, the driving force behind the segregation is the minimization of the total energy of the crystal (the change in the chemical potential) and is given by

$$\Delta \mu_i^{(j+1,j)} = (\mu_i^{(j+1)} - \mu_i^{(j)}) - (\mu_m^{(j+1)} - \mu_m^{(j)}) \quad (4)$$

where $\mu_i^{(j+1)}$ is the chemical potential of impurity i in layer $j + 1$ and $\mu_m^{(j+1)}$ is the chemical potential of the bulk atom m in layer $j + 1$.

In the modified Darken model the concentration change of impurity i between the $(j + 1)$ -th layer and the j -th layer of the crystal as function of time is given by

$$\frac{\partial X_i^{(j)}}{\partial t} = \left[\frac{M_i^{(j+1 \rightarrow j)} X_i^{(j+1)}}{d^2} \Delta \mu_i^{(j+1 \rightarrow j)} - \frac{M_i^{(j \rightarrow j-1)} X_i^{(j)}}{d^2} \Delta \mu_i^{(j \rightarrow j-1)} \right] \quad (5)$$

where $M_i = D_i/RT$ is the mobility of the segregating impurity i in the bulk for a dilute alloy, D is the diffusion coefficient and d is the thickness of the segregated layer.

Using the modified Darken model (equation 5), the entire segregation profile can be calculated and a set of segregation parameters can be extracted.

3. Experimental details

Cu crystals (0.70 mm thick and 10 mm diameter) with a S bulk concentration of 0.0008 at% (8 ppm) were obtained from a high purity (99.99 %) polycrystalline Cu. The Cu crystals were doped with a low concentration of In of 0.059 at%. A detailed Cu(0.059 at% In) alloy preparation procedure will be published. One side of the doped crystal was chosen as the front side and was mechanically polished to 0.05 μm using a diamond suspension solution. The crystal was further mounted on a heater inside the ultra high vacuum (UHV) chamber ($P = 1.0 \times 10^{-9}$ Torr). The crystal temperature was measured directly from the back of the crystal with a chromel–alumel thermocouple (Type K) and the measured temperature was calibrated in terms of the true surface temperature of the crystal. AES was used to monitor the surface of the crystal (polished side of the crystal) during linear heating of the crystal. A 5.0 keV primary electron beam with a current of 0.7 μA was used for the AES measurements and the modulation energy was 2.0 eV. The scan rate was 5.0 eV/s and the time constant was 0.1 s. The ion gun used for sputter cleaning was operated at a beam energy of 2.0 keV, an argon pressure of 1.5×10^{-5} Torr and the beam was rastered over a 2 mm \times 2 mm area. The crystal was tilted with the normal of the crystal surface at a 30° angle with respect to the direction of the incident electron beam.

Before the segregation run the crystal was pre-heated at 1073 K for 24 hours and cooled to 373 K at a cooling rate of -0.05 K/s to restore the initial condition of the crystal (uniform bulk concentration). The crystal was pre-heated at $T_0 = 373$ K for 1 hour and sputter cleaned for exactly 30 s. Immediately after sputtering Auger peak to peak heights (APPHs) were recorded as a function of time for Cu (922 eV), S (153 eV) and In (405 eV) as the crystal temperature, T , was increased linearly with time at a constant heating rate, α , of 0.05 K/s from 373 K to 1073 K. In this regard the time, t , scale is converted to temperature, T , using the relation given by

$$T = T_0 + \alpha t \quad (6)$$

The APPH data was quantified using the method discussed in the appendix of Ref. [10] and the sensitivity factors were determined from the pure elemental standards under the same conditions. In the quantification, the backscattering factor from Shimizu as discussed by Seah [11], the inelastic mean free path (IMFP) calculated with the TPP-2M formula [12] were used. The Auger spectra of the crystal were obtained and showed only the segregation of In and S.

4. Results and Discussion

Figure 1 shows the surface enrichment of In and S from a dilute Cu(In,S) ternary alloy which was obtained by using a linear heating method at a heating rate of 0.05 K/s. In figure 1 four different regions are shown: Region A, the crystal temperatures are low and the bulk diffusion coefficients (D) of In and S are low, hence In and S do not enrich the surface layer of the crystal. Region B, (the In kinetic region) In segregated to the surface and reached a maximum surface concentration of 25 %. Region C, (the S kinetic region) the segregation rate of S increased, thus increasing the surface concentration of S. As S segregated to the surface, it replaced the In from the surface layer. Region D, (the equilibrium region) S reached a maximum surface concentration of 30 % and the In maximum surface concentration reached almost 0 % after being replaced by S.

The maximum surface concentrations of In and S are determined by the segregation and interaction energies. According to the Guttman model, a large difference between the segregation energies for segregating impurities leads to a behaviour whereby an impurity with greater segregation energy (more negative) replaces the one with lesser segregation energy (less negative). Therefore, The In replacement by S could be as a result of the segregation energy for S that could be greater (more negative) than that for In. Swart et. al. [13] have demonstrated that a repulsive interaction between two segregating impurities (In and S in this study) lead to a higher equilibrium concentration of impurity 2 (S in this study) and a lower equilibrium concentration of impurity 1 (In in this study). Therefore, the interaction between the In and S atoms could be repulsive.

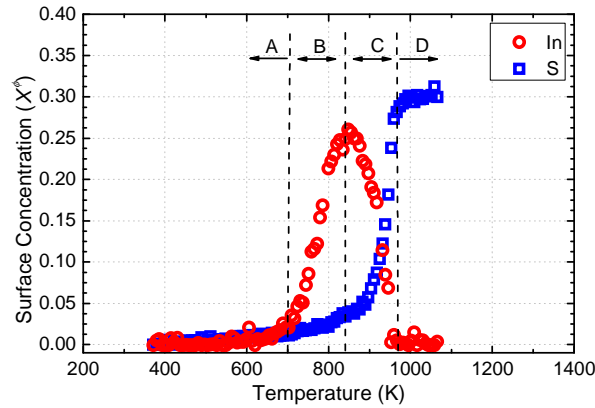


Figure 1. The surface enrichment of In and S from a Cu(In,S) ternary alloy obtained at a heating rate of 0.05 K/s.

The surface concentration scale in figure 1 was converted to the enrichment factor (β) (discussed in the theory section above) as shown in figure 2. The modified semi-infinite model of Fick (equation 1) was fitted through the In kinetic region (region B in figure 1) and the S kinetic region (region C in figure 1) of the segregation profiles and from the best fits (shown in figure 2) the D_0 and the Q values were extracted (see the insert text of figure 2).

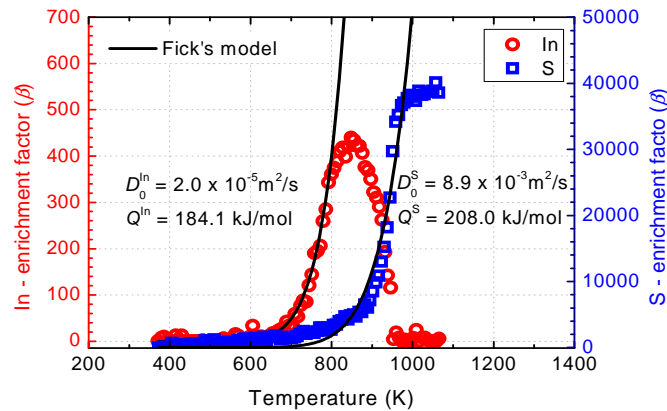


Figure 2. The enrichment factor (β) for In and S segregation from a Cu(In,S) alloy obtained at a heating rate of 0.05 K/s.

The Guttman model (equation 2 and 3) was fitted through the equilibrium region (region D in figure 1) of the In and S segregation profiles and from the best fits (shown in figure 3) the ΔG and the Ω values were extracted (see the insert text of figure 3).

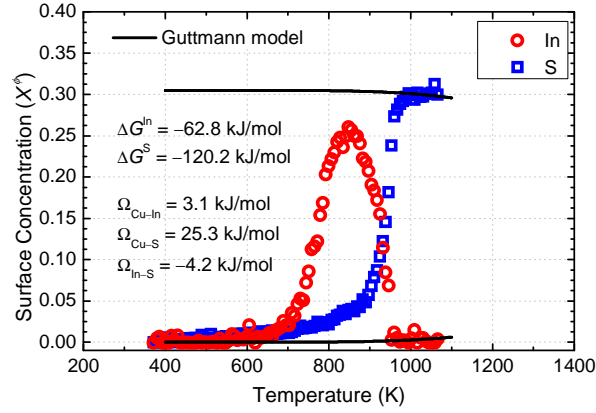


Figure 3. The surface enrichment of In and S from a dilute Cu(In,S) ternary alloy fitted with Guttman model (solid lines).

Furthermore, using the values of the parameters D_0 , Q , ΔG and Ω extracted from the best fits of the Fick's and Guttman model as the initial parameters in the Darken calculations (equation 5), the profiles that best simulate the measured segregation profiles were calculated (see figure 4). The parameters of the Darken calculations shown in figure 4 are listed in table 1.

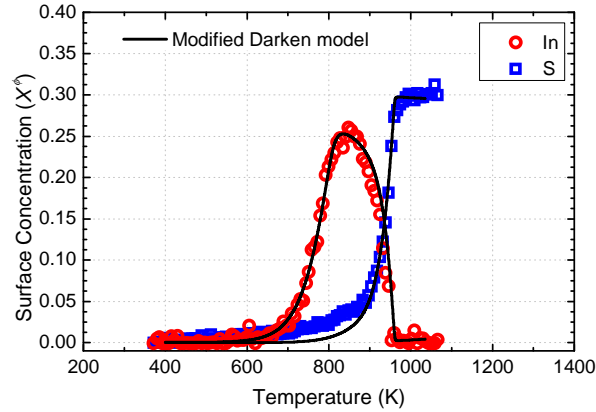


Figure 4. The surface enrichment of In and S from a Cu(In,S) alloy. The solid lines are calculated with the Darken model.

Table 1. In and S segregation parameters extracted from the modified Darken model (figure 4). The interaction energy for In and S (Ω_{In-S}) is -4.0 ± 0.5 kJ/mol. X in Ω_{X-Cu} denotes either In or S.

Segregated Impurities	Segregation parameters			
	D_0 (m ² /s)	Q (kJ/mol)	ΔG (kJ/mol)	Ω_{X-Cu} (kJ/mol)
In	$(2.2 \pm 0.5) \times 10^{-5}$	184.3 ± 1.0	-62.8 ± 1.4	3.0 ± 0.4
S	$(8.8 \pm 0.5) \times 10^{-3}$	213.0 ± 3.0	-120.0 ± 3.5	23.0 ± 2.0

In table 1 it is clear that the activation energy (Q) and the pre-exponential factor (D_0) for In bulk diffusion are smaller than for S. Therefore, S diffuses faster in the bulk than In. The activation energy for In ($Q = 184.3$ kJ/mol) is lower than that for S ($Q = 213.0$ kJ/mol) hence In segregates first (before S) at low crystal temperatures. In addition, a higher bulk concentration of In (0.059 at%), which is much higher than that of S (0.0008 at%), increases the segregation rate of In at low crystal temperatures. The attractive interaction between the In and Cu atoms ($\Omega_{\text{Cu-In}} = 3.0$ kJ/mol) set a preference for unlike first-neighbour bonds formation between the In and Cu atoms and that suggest that an In atom prefers to be surrounded by Cu atoms in the Cu(In) system. Similarly, the attractive interaction between the S and Cu atoms ($\Omega_{\text{Cu-S}} = 23.0$ kJ/mol) set a preference for unlike first-neighbour bonds formation between the S and Cu atoms. The repulsive interaction between the In and S atoms ($\Omega_{\text{In-S}} = -4.0$ kJ/mol) shows less or no tendency of In-S atomic bonds formation. There is a large difference in the segregation energies for In ($\Delta G = -62.8$ kJ/mol) and S ($\Delta G = -120.0$ kJ/mol) and that elaborates the displacement of In in the surface layer by S (the segregation of S is more energetically favourable than that of In).

5. Conclusion

The segregation behaviour of In in a Cu crystal was observed. S (regular impurity in a Cu crystal) was also observed to segregate with In. From the measured segregation profiles, the segregation parameters were successfully obtained for In and S segregation in a Cu crystal using the linear heating method. The segregation data for In segregation in Cu crystal was not found in literature; hence the results of this study are not compared to literature findings. However, the pre-exponential factor ($D_0 = 8.8 \times 10^{-3}$ m²/s) and the activation energy ($Q = 213.0$ kJ/mol) obtained in this study for S segregation in a Cu crystal are in good agreement with those reported by Viljoen et al. [4] ($D_0 = 1.8 \times 10^{-3}$ m²/s and $Q = 212.0$ kJ/mol obtained using the linear heating method). In this study, processes such as grain boundary diffusion, segregation at grain boundaries, the segregation dependence of different grain surface orientations, segregation from bulk and grain boundaries could not be separated from each other. Therefore, the segregation parameters obtained in this study take all active processes into account and yields average results.

Acknowledgments

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