AES and TOF-SIMS measurements of In segregation in a polycrystalline Cu crystal

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Abstract. The bulk-to-surface segregation of In impurity in a polycrystalline Cu crystal was measured using Auger Electron Spectroscopy (AES) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) coupled with a programmable heater. AES segregation measurements were carried out using constant temperatures in the temperature range 733 K to 853 K. The measured AES data showed that In segregate to the surface and it has reached a relative high surface concentration on the Cu surface. The AES In segregation data was fitted with the semi-infinite model of Fick's equation to obtain the In bulk diffusion parameters ($D_0 = 1.1 \times 10^{-5}$ m^2 s^{-1}, $Q = 191.9$ kJ mol^{-1}). In a polycrystalline Cu crystal, segregation measurements could be affected by the surface orientation of the different grains. The effect that the surface orientation of the grains has on the In segregation was obtained with TOF-SIMS measurements (carried out using the linear temperatures method). The TOF-SIMS In segregation data from two twin grains showed equal segregation rates, which is expected since the twin grains have the same surface orientation. However, segregation data from two different grains showed different segregation rates which confirm the effect surface orientation has on segregation.

1. Introduction

The Cu-In system receives attention particularly for applications in solar cells, thin-film transistor liquid-crystal display, ultra-large-scale integrated devices [1–3]. In surface and interface science, the properties of a surface layer of a crystal can be modified such that they differ significantly from that of the bulk layers especially in elemental composition. Similarly, a grain boundary composition can be modified such that it differs significantly from that of the grain/bulk layers. Such modification in surface and grain boundary composition could be attained through a diffusion and segregation process (that results from a heat treatment of a crystal). A crystal containing active impurities (with a negligible bulk concentration), if is heat treated at a relatively high temperature the impurities accumulates on the surface and grain boundaries of a crystal as a result of the segregation process [4]. In some of these crystals, not only segregation of impurities occurs during heat treatment but also twinning (i.e. twin boundaries) that also occurs during crystal deformation [5]. In a polycrystalline crystal, a single grain without twinning has identical surface orientation of atoms arrangements (Figure

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1). However, for adjoining grains the surface orientation differs from grain to grain. For a single grain with twin boundaries the surface orientation for twin grains is identical, what is observed is a special mirror image misorientation of the initial lattice structure (see figure 1) [5]. It has been shown in literature that segregation kinetics depends on the grain/surface orientation of the crystal [6, 7]. In support of literature, segregation kinetics measurements on different grains with probably different surface orientations are fascinating aspects to investigate.

In this study, the focus is on measuring the bulk-to-surface segregation of In impurity in a polycrystalline Cu crystal using Auger Electron Spectroscopy (AES) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) coupled with a programmable heater. Note that studies on In segregating from the bulk to the surface and grain boundaries of a Cu crystal are lacking in literature. The AES In segregation data (carried out using the constant temperatures) was fitted with the semi-infinite model of Fick to obtain the In bulk diffusion parameters, namely the pre-exponential factor (D_0) and the activation energy (Q). The effect that the surface orientation of the grains has on the In segregation was also obtained with TOF-SIMS measurements (carried out using the linear temperatures method).
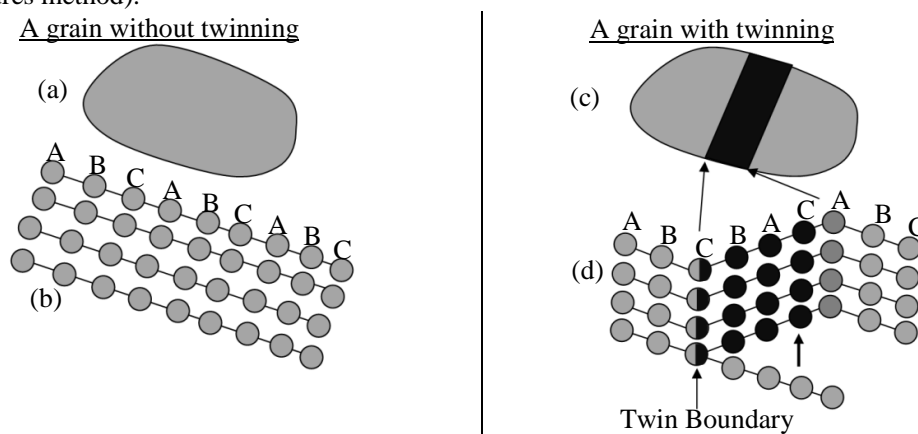
Figure 1. The schematic diagrams of (a) a grain without twin boundaries ((b) has identical surface orientation of atoms arrangements); (c) for a grain divided into twin grains by twin boundary ((d) a special mirror image misorientation of the initial lattice structure is observed [5]).

2. 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 0.06 at%. The detailed Cu(0.06 at% In) alloy preparation procedure is published elsewhere [8].

An In doped Cu crystal was mounted on a heater inside the AES ultra high vacuum chamber. AES was used to monitor the polished surface (mechanically polished to 0.05 μm using a diamond suspension solution) of the crystal during constant heating of the crystal. AES constant temperature measurements were recorded for Cu (922 eV), S (153 eV) and In (405 eV) for temperatures 733 K; 763 K; 793 K; 823 K and 853 K. For each temperature, a crystal was heated for 1 h to establish a thermal equilibrium then sputtered over a 2000×2000 μm² area for 30 s. The Auger spectra of the crystal were obtained and showed only the segregation of In and S.

Furthermore, an In doped Cu crystal was mounted on a programmable heater inside the TOF-SIMS ultra high vacuum chamber. TOF-SIMS measurements were recorded (from a crystal polished surface) for In impurity segregation from a Cu crystal using a 30 keV Bi_1^+ Ion beam and linear temperature ramp at a heating rate of 0.05 K/s. Measurements were performed in a positive polarity. Before each segregation measurement the crystal surface was sputtered over a 700×700 μm² area using a 2 keV O_2^+ Ion beam.

3. Results and Discussion

The AES segregation measurements were performed in the middle of a grain on the surface as shown (with a marker A) in the insert of figure 2. Figure 2, shows the surface enrichment of In and S from an In doped polycrystalline Cu crystal, which was obtained from the constant temperature measurements at 733 K. In figure 2, two distinctive regions (looking at In data) are shown: In region A (kinetic region), it can be seen that initially In segregated to the surface at a higher segregation rate. However, in region B the segregation rate of In decreased significantly. From the measured AES segregation data, S (a common Cu impurity) was also observed to segregate with In. A high segregation rate of In could be as a result of a higher In bulk concentration (0.06 at%) and the bulk diffusion coefficient (D). Since, the segregation rate is limited by the change in the chemical potential ($\Delta\mu$) (i.e. a function of the impurities bulk concentration) and the bulk diffusion coefficient is characterized by inherent activation energy (that could be lower to give a higher diffusion coefficient) and the pre-exponential factor. The effects of the bulk concentration (X^B) and the bulk diffusion coefficient (D) on segregation kinetics are brought together by the semi-infinite model of Fick that best describe the kinetics of segregation.
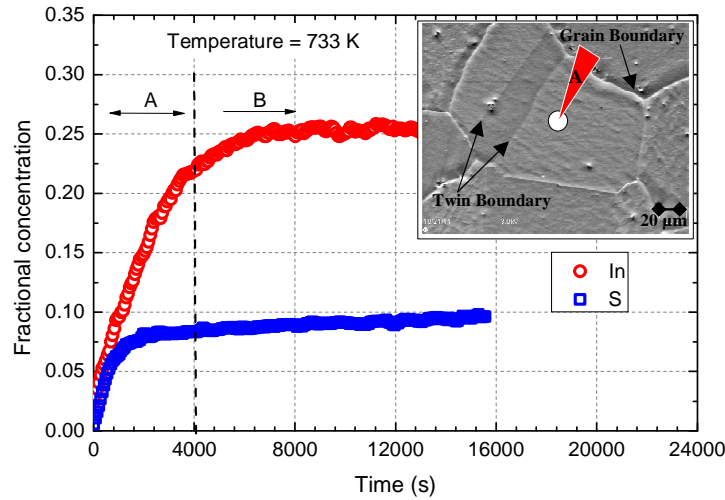
Figure 2. AES In and S segregation data measured at a constant temperature of 733 K. The insert is the secondary electron detector micro image of a polycrystalline Cu crystal surface that demonstrates a spot A used for the segregation measurements.
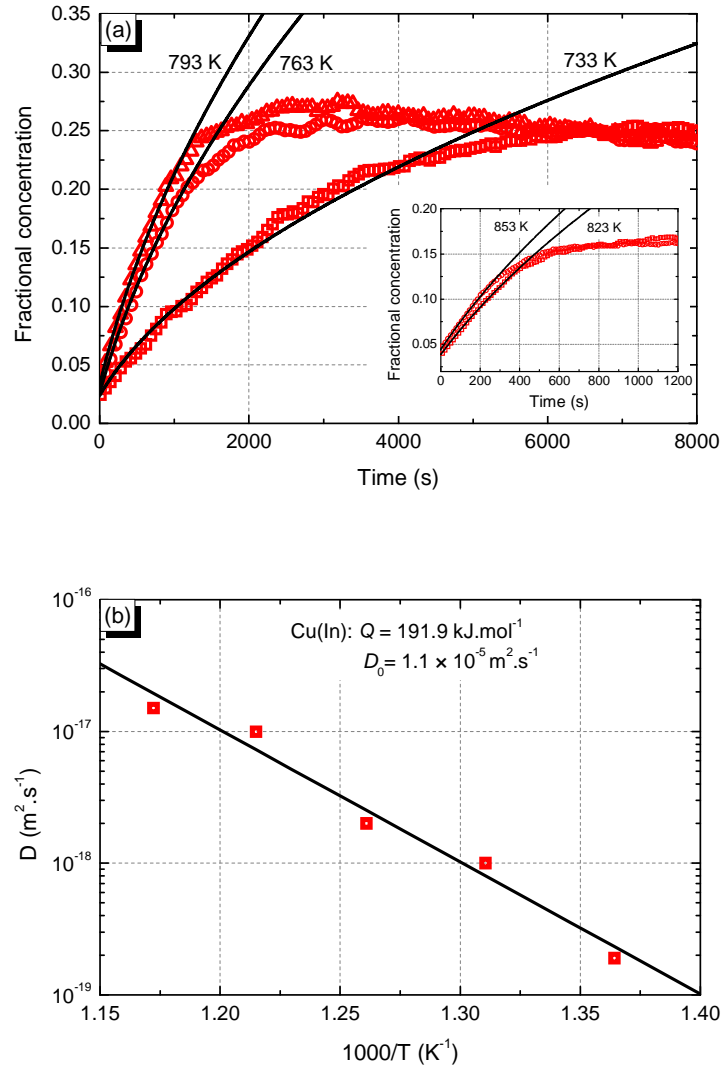
The semi-infinite model of Fick for surface concentration (X^ϕ) of segregating impurities with time (t) (also adapted to account for the sputter depletion after sputtering for time (t_0) is given by the following expression [9–10]:

$$X^\phi = X_0^\phi + X^B\left[1 + \frac{2}{d}\left(\frac{D(t+t_0)}{\pi}\right)^{1/2}\right] - X^B\left[\frac{2}{d}\left(\frac{Dt_0}{\pi}\right)^{1/2}\right]$$

(1)

where X_0^ϕ is the number of segregated impurities that were not sputtered, X^B is the impurity bulk concentration, d is the thickness of the segregated layer and $D = D_0 \exp(-Q/RT)$ is a diffusion coefficient with activation energy Q and pre-exponential factor D_0 at a constant temperature T.

The data points of the kinetics of segregation (region A in figure 2) of In measured from a In doped polycrystalline Cu crystal at constant temperatures of 733 K; 763 K; 793 K; 823 K and 853 K were fitted with equation 1 adjusting a parameter D as shown in figure 3(a). Fitted D values were plotted as

shown in figure 3(b) and from a plot the pre-exponential factor and the activation energy ($D_0 = 1.1 \times 10^{-5}$ m^2 s^{-1}, $Q = 191.9$ kJ mol^{-1}) were extracted for In bulk diffusion in the Cu crystal.


Figure 3. (a) In segregation data measured from a In doped polycrystalline Cu crystal at a constant temperatures of 733 K; 763 K; 793 K; 823 K and 853 K. The solid lines are the best fits of the semi-infinite model of Fick. (b) Arrhenius plot of fitted D values.

The bulk diffusion parameters ($D_0 = 1.1 \times 10^{-5}$ m^2 s^{-1}, $Q = 191.9$ kJ mol^{-1}) of In segregation in Cu crystal obtained from this study using the constant temperature method compare well with those obtained from the same crystal using the linear temperature method ($D_0 = 1.8 \times 10^{-5}$ m^2 s^{-1}, $Q = 184.3$ kJ mol^{-1}) [12].

The In bulk diffusion parameters obtained in this study could be affected by the surface orientation of the different grains, since they were extracted from the segregations kinetics. It is known in literature that segregation kinetics depends on the grain/surface orientation of the crystal [6, 7]. The effect that the surface orientation of the grains has on the In segregation

was obtained with TOF-SIMS measurements (see figure 4). From the insert of figure 4, it can be seen from the elemental map that the In segregated from the bulk to the grain boundaries and grain surfaces. The TOF-SIMS In segregation data from two twin grains (indicated with a marker A and B in figure 4(a) insert) showed equal segregation rates (from low crystal temperatures up to 520 K as shown in figure 4(a)), which is expected since the twin grains have the same surface orientation. However, segregation data from two different main grains showed different segregation rates (see figure 4(b)) which confirm the effect surface orientation has on segregation kinetics. Clearly, these suggest that the In bulk diffusion parameters obtained in this study will differ significantly between grains with different surface orientations. However, the parameters could be comparable.
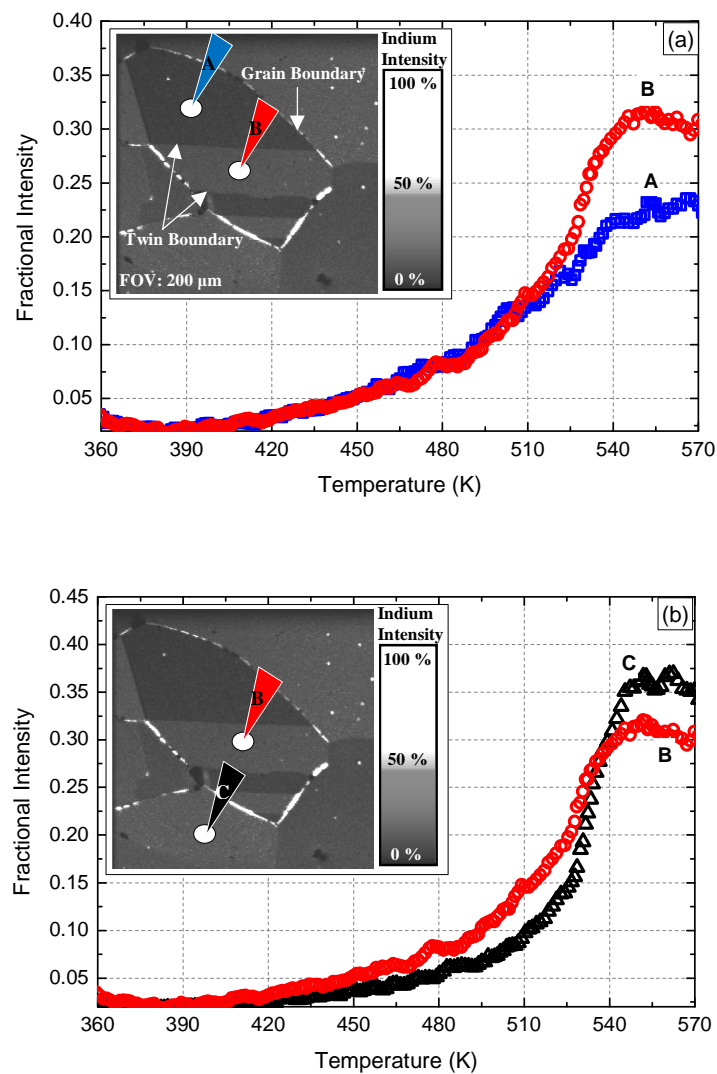
Figure 4. TOF-SIMS In segregation data of a linear heat run measured at different positions (A–C) on the Cu surface. The insert is a TOF-SIMS elemental map of the In segregation on the surface of the Cu crystal after annealing.

It should be mentioned that in TOF-SIMS measurements the segregation of other impurity such as K was measured at higher temperatures (> 520 K), and as its concentration increased on the surface it strongly interacted with In on the surface causing In desegregation.

The large difference as seen in the maximum surface intensities from the two twin grains (Figure 4(a)) could be related to the impurities interaction energies according to the Guttmann model (that relates the maximum surface concentrations to the impurities segregation and interaction energies) [13]. Nevertheless, such a large difference in the intensities could not be related to impurities interaction energies (because the twin grains have the same surface orientation and the same impurities were measured from either grain). A high intensity in figure 4(a) suggested that there is more of In impurity in the twin grain marked B in figure 4(a) (as compared to the adjacent twin grain).

4. Conclusion

In this study, the bulk-to-surface segregation of In impurity in a polycrystalline Cu crystal was measured using AES and TOF-SIMS coupled with a programmable heater. From the measured AES data the In bulk diffusion parameters ($D_0 = 1.1 \times 10^{-5}$ m^2 s^{-1}, $Q = 191.9$ kJ mol^{-1}) were obtained. The In bulk diffusion parameters obtained in this study compare well with those obtained from the same crystal using the linear temperature method ($D_0 = 1.8 \times 10^{-5}$ m^2 s^{-1}, $Q = 184.3$ kJ mol^{-1}) [12]. Since measurements were carried out from a polycrystalline crystal, the effect that the surface orientation of the grains has on the In segregation was obtained with TOF-SIMS measurements. The TOF-SIMS segregation data from two twin grains showed equal segregation rates, which is expected since the twin grains have the same surface orientation. The TOF-SIMS segregation data from two different grains showed different segregation rates which confirm the effect surface orientation has on segregation data. Therefore, In bulk diffusion parameters obtained in this study could be expected to differ significantly if measured on a different grain with a different surface orientation.

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