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Determination of grain-boundary diffusion coefficients by Auger electron spectroscopy

Z. Erdélyi [a,b], Ch. Girardeaux [a,*], G.A. Langer [b], L. Daróczi [b], A. Rolland [a], D.L. Beke [b]

[a] Laboratoire de Métallurgie, UMR 6518, Faculte des Sciences de St. Jerome, Université Aix-Marseille III, case 511, 13397 Marseille Cédex 20, France

[b] Department of Solid State Physics, L. Kossuth University, PO Box 2, 4010 Debrecen, Hungary

Abstract

Surface accumulation method, called the Hwang–Balluffi method [J.C.M. Hwang, J.D. Pan and R.W. Balluffi, J. Appl. Phys., 50(3), 1979, 1339], was applied to measure the grain-boundary diffusion of Ag at low temperatures (413 and 428 K) in a nanocrystalline Cu film. Ag atoms from the Ag layer diffused through the copper nanocrystalline film along the grain boundaries to the opposite surface (i.e. the accumulation surface) where they spread out by rapid surface diffusion and accumulated. The rate of accumulation was detected by Auger Electron Spectroscopy (AES). It was shown that the results are not sensitive to the supposition whether accumulation takes place in one or two monolayers of the surface. TEM observations have been made in the same time before and after heat treatment to check the stability of the nanostructure.

PACS: 64.75 = segregation; 66.30 = Diffusion in Solids

Keywords: Grain-boundary; Diffusion coefficient; AES; Hwang–Balluffi method

1. Introduction

Investigations of grain-boundary diffusion are essential for the understanding of metallurgical properties of metals. During the last few decades surface and grain-boundary segregation phenomena have been studied in large detail using many different experimental techniques of surface analysis and very sophisticated theoretical methods as well [2–7]. Furthermore, the control of the grain-boundary diffusion coefficient (D_b) becomes very important at low temperatures, where grain-boundary diffusion is the rate-controlling mechanism of mass transport (mechanism of diffusion can be orders of magnitude faster than lattice diffusion) [8]. A reduction in the D_b diffusivity is very helpful for enhancing the lifetimes of thin film interconnected in microelectronic devices, where the destructive electromigration effect is predominately related to the atomic mobility in the grain boundaries [9]. Therefore, it is very important to study in detail mass transport data in nanocrystalline films, which is, up to now, not well known. In this paper, we applied a surface accumulation method called the Hwang–Balluffi method [1] to measure the

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[*] Corresponding author.

E-mail address: christophe.girardeaux@edifis.u-3mrs.fr (Ch. Girardeaux).

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grain-boundary diffusion at low temperature in a nanocrystalline Cu film. Ag atoms from the Ag layer diffused through the copper nanocrystalline film along the grain boundaries to the opposite surface (i.e. the accumulation surface) where they spread out by rapid surface diffusion and accumulated. The rate of accumulation was detected by Auger Electron Spectroscopy (AES). This technique is a highly sensitive method for measuring grain-boundary diffusion since the grain-boundary diffusion distance is short and the number of grain boundaries is large (interest in using nanocrystalline films). Thanks to this technique it was, therefore, possible to measure the grain-boundary diffusivity at unusually low temperatures. This, as we will see, offers a possibility to measure grain-boundary diffusion in nanocrystalline systems, without significant recrystallization. The other aim of this work was to analyze the sensitivity of the results on the suppositions of the atomic details of the surface accumulation. We will illustrate that the results are not very different for the cases when one or two top monolayers accumulation mechanism is supposed in fitting the measured data.

2. Experimental procedure

The Ag/Cu bilayers were prepared by DC magnetron sputtering. The HV sputtering system has been described in detail elsewhere [10]. The base and argon pressure was 5×10^{-7} and 7×10^{-3} mbar, respectively, the distance between the target and the substrates was 10 cm and the typical sputtering rates were 0.5 nm/s for Ag (50 W, 350 V DC) and 0.35 nm/s (90 W, 314 V DC) for Cu (the sputtering rates were calibrated using an INFICON quartz crystal microbalance). Silicon-oxide wafers were used as substrate and the purity of targets of Ag and Cu was 99.99%. First, a 12-nm-thick Ag layer was deposited onto the SiO_2 substrate then a 21-nm-thick Cu nanocrystalline layer onto the Ag layer.

A Jeol 2000 FX-II TEM was used to check the grain size of the copper layer before and after heat treatment.

2.1. AES

The sample was mounted in a conventional UHV chamber ($P < 1 \times 10^{-9}$ Torr) equipped with a three-gird LEED optics, an ion gun (Ribber ACI30) and a CMA (Ribber OPC105) with a coaxial gun. The gun was usually operated with an electron beam of 2 keV and 60 μA. A 4-eV modulation tension was used to obtain the derivative spectrum $\mathrm{d}N(E)/\mathrm{d}E$. The sample was fixed on a heater (carbon furnace encapsulated in a boron nitride ceramic), which presents 5 degrees of liberty (X, Y, Z and two rotational movements). This heater is monitored by an Eurotherm regulator (902P) and the temperature controlled by a Pt–PtRh thermocouple fixed on the surface of the sample. In the present work, the surface concentrations of silver and copper were monitored by following the behavior of the 356 eV silver Auger peak and the 60 and 920 eV copper peaks as a function of annealing time. The peak heights were obtained by the usual procedure of measuring the difference of intensity from the most negative point (from where the kinetic energy is measured) to the most positive point on each peak of the derivative spectrum. To minimize the instrumental errors, the measured peak heights were reduced to a peak height ratio, q, through the formula

$$q = \frac{I_{356}/I_{356}^{0}}{I_{920}/I_{920}^{0}} = \frac{I_{356}}{I_{920}} S, \qquad (1)$$

where the superscript zero designates the pure element in the bulk form and S is the so-called relative Auger sensitivity factor (for the present experiment we measured $S = I_{920}^{0}/I_{356}^{0} = 0.26$). This q parameter represents the buildup of silver on the surface that is why it can be called surface accumulation parameter.

Before heat treatment, a survey spectrum of the samples was recorded to check the ‘‘cleanness’’ of the surface. Since oxygen and carbon contamination were observed systematically, a rather low Ar^{+} sputtering (ions being accelerated to 2 keV with current densities of 70 $\mu A\ cm^{-2}$) of the surface was applied. The ‘‘cleaned’’ surface presented, however, a remaining low carbon contamination. In our experiment, the possible buildup of carbon during heat treatment was monitored by measuring survey spectra at several annealing times. It is believed that the carbon contamination was maintained at a sufficiently low level so that the surface diffusion on the accumulation surface was not affected significantly by adsorption of CO, O_2, CO_2 and CH_4 molecules.

3. Theory

3.1. Diffusion model

Hwang et al. [1] analyzed the problem of diffusion in an array of uniformly spaced parallel grain boundaries in a thin-film system under the conditions of C kinetics. In this regime, volume diffusion is essentially frozen out so that the material transport takes place only within the grain boundaries without any leakage into the adjoining grains. The geometry of the thin-film system analyzed is illustrated in Fig. 1.

Hwang and Balluffi developed a mathematical analysis for interpretation of the accumulation kinetics measurements. They built a model of the surface region in which it was assumed that the segregated atoms could be distributed in the surface region to a depth corresponding to at least several atomic layers. Moreover, the grain boundaries, as usual, were rectangular slabs (of width δ) normal to the two surfaces of the film, h being the thickness of the layer (Fig. 1).

The Hwang–Balluffi equation [1] was used to determine the D_b grain-boundary diffusion coefficient from the time dependence of the c_s average concentration at the accumulation surface.

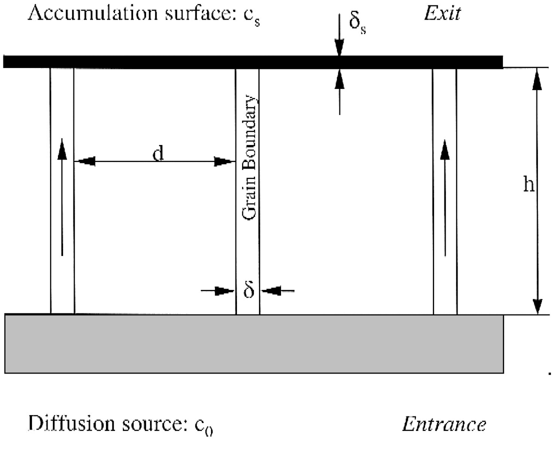

Fig. 1. Geometry of the parallel-boundaries thin film system used in the Hwang–Balluffi method.

$$c_s/c_0 = [1 - \exp(-\alpha t')] \tag{2}$$

$$\alpha = \delta D_b \lambda / \delta_s h, \tag{3}$$

where δ_s is the thickness of the segregated layer and λ the grain-boundary density (in our case, for a polycrystal having cubic grains of width d, $\lambda = 2/d$). Here, the quantity t' is a ‘‘corrected time’’ of the form

$$t' = t - t_0, \tag{4}$$

where t_0 is a constant, which takes into account the fact that a transient phenomenon occurred in each diffusion run before a quasi-steady-state was reached. It was shown [1] that this equation should be applied under the following conditions: (i) a quasi-steady-state grain-boundary diffusion current to the accumulation surface has been established; (ii) the surface diffusion rate is sufficiently rapid so that the silver is uniformly distributed laterally in the surface region; (iii) a constant concentration of pure silver is maintained in the grain-boundary at the silver source; and (iv) the ratio surface/grain-boundary segregation is unity.

3.2. Surface accumulation parameter

The value of q predicted by this model is sensitive to the details of the segregated atom distribution since the Auger electrons corresponding to the three peaks possessed widely different Inelastic Mean Free Path (IMFP). For example, Hwang et al. [1] mentioned that — due also to the carbon contamination of the surface — the accumulation takes place probably not only in the top monolayer. In their concrete calculations for Ag grain-boundary diffusion in Au, they supposed that this surface homogenization set in the top two monolayers. Related to this point there are two questions which are worth to be analyzed. First, developing on whether one or two monolayers are considered, is the δ/δ_s ratio different? Second, if the AES is used, are the results obtained for D_b sensitive whether one or two monolayer-accumulation is supposed? These questions will be considered in detail in this section.

In the case of a homogeneous specimen containing n layers, the measured Auger intensity can be given by the following formula [11]

$$I_n = I_1 + \alpha I_1 + \alpha^2 I_1 + \ldots + \alpha^{n-1} I_1$$
$$= (1 + \alpha + \ldots + \alpha^{n-1}) I_1 = \frac{1-\alpha^n}{1-\alpha} I_1, \qquad (5)$$

where I_1 is that part of the total intensity that would come from each layer without attenuation. But the Auger electrons coming from the bulk (not from the surface layer) were attenuated by the top layers, (α is the attenuation coefficient). If $n \to \infty$, i.e. for a bulk specimen, the Auger intensity is

$$I_\infty = \lim_{n\infty} I_n = \frac{I_1}{1-\alpha} \Rightarrow I_1 = (1-\alpha) I_\infty. \qquad (6)$$

Using Eqs. (5) and (6), the Auger intensity coming from a homogeneous specimen containing n layers (or the part of the total intensity which come from the n top layers of a homogeneous bulk specimen) is

$$I_n = (1-\alpha^n) I_\infty. \qquad (7)$$

The concentration of A atoms in an AB bulk alloy can be defined by the following way

$$c = I^{\mathrm{A}}_{\mathrm{AB},\infty} / I_{\mathrm{A},\infty}, \qquad (8)$$

where $I^{\mathrm{A}}_{\mathrm{AB},\infty}$ and $I_{\mathrm{A},\infty}$ are the Auger intensity coming from the A atoms of the bulk alloy and the Auger intensity coming from the bulk specimen containing only A atoms, respectively. In terms of this definition, it is also possible to determine the concentration of A and B atoms in n AB homogeneous surface layers deposited on a pure B substrate

$$c = I^{\mathrm{A}}_{\mathrm{AB},n} / I_{\mathrm{A},n}. \qquad (9)$$

Since the substrate does not contain A atoms, $I^{\mathrm{A}}_{\mathrm{AB},n}$ is equal to the I_{A} measured intensity coming from the A atoms of the whole specimen. Using Eq. (3), the concentration of A atoms is

$$c = \frac{I_{\mathrm{A}}}{I_{\mathrm{A},n}} = \frac{I_{\mathrm{A}}}{(1-\alpha^n_{\mathrm{A}}) I_{\mathrm{A},\infty}}. \qquad (10)$$

The concentration of B atoms is

$$1 - c = I^{\mathrm{A}}_{\mathrm{AB},n} / I_{\mathrm{B},n}. \qquad (11)$$

But, in the case of the calculation of the concentration of B atoms, it is necessary to take into account the $I_{\mathrm{B},n+1\ldots\infty}$ contribution of the substrate ($I^{\mathrm{B}}_{\mathrm{AB},n}$) as well, which is not equal to the I_{B} measured intensity coming from the B atoms of the whole specimen:

$$I - c = \frac{I_{\mathrm{B}} - I_{\mathrm{B},n+1\ldots\infty}}{I_{\mathrm{B},n}} = \frac{I_{\mathrm{B}} - \alpha^n_{\mathrm{B}} I_{\mathrm{B},\infty}}{(1-\alpha^n_{\mathrm{B}}) I_{\mathrm{B},\infty}},$$
$$\left(I_{\mathrm{B},n+1\ldots\infty} = I_{\mathrm{B},\infty} - I_{\mathrm{B},n} = I_{\mathrm{B},\infty} - (1-\alpha^n_{\mathrm{B}}) \times I_{\mathrm{B},\infty} = \alpha^n_{\mathrm{B}} I_{\mathrm{B},\infty} \right). \qquad (12)$$

Using the definition of q and Eqs. (10) and (12), the surface accumulation parameter for n accumulated layers is

$$q_n = \frac{I_{\mathrm{A}}/I_{\mathrm{A},\infty}}{I_{\mathrm{B}}/I_{\mathrm{B},\infty}} = \frac{c(1-\alpha^n_{\mathrm{A}})}{1 - c(1-\alpha^n_{\mathrm{B}})}. \qquad (13)$$

Using the usual form of the attenuation parameter

$$\alpha_i = \exp[-1/(\lambda_i \cos\omega)] \qquad i = \mathrm{A,B}, \qquad (14)$$

where λ_i is the IMFP (in monolayer units), and ω is the emission angle of Auger electrons, Eq. (13) in the two layers limit is the same as the one that was used by Hwang et al. (see Eq. (2) in Ref. [1]).

4. Results and discussion

Twenty years ago, Gibson and Dobson [12] described that annealing of thin (10–20 nm) epitaxial films of nickel or copper grown on silver(111) at 300°C produced drastic changes in the morphology of the Ni or Cu layers. The flat deposits contracted into three-dimensional islands. In our experiments, TEM was used to check the grain size of the nanocrystalline copper layer before (Fig. 2) and after (Fig. 3) heat treatment at 413 and 428 K. It is shown in Fig. 2 (before annealing) that the grain size of the Cu deposited films corresponds to the thickness of the Cu deposited layer, i.e. around 20 nm. The Ag/Cu couple was annealed at sufficiently low temperatures (413 and 428 K — Fig. 3) so that the structure was frozen out (the copper grains size remained unchanged (around 20 nm) after annealing), and the diffusion then occurred along the grain boundaries.

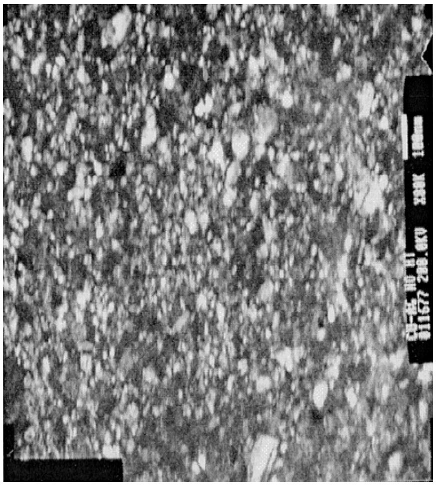

Fig. 2. Dark field TEM image before heat treatment at 428 K (scale,—: 50 nm).

AES can be applied for grain-boundary diffusion studies using the surface accumulation method based on the observation of surface accumulation of the diffusing atoms on the terminal surface of the sample [1,13]. However, this method can be affected by the presence of even small amounts of impurities, disturbing the velocity of the surface diffusion [14].

A typical evolution of the 356 eV silver Auger peak and the 60 and 920 eV copper peaks as a function of annealing time is shown in Fig. 4, and the time evolution of c_s fitted by Eq. (13) for $n = 1$ in Fig. 5.

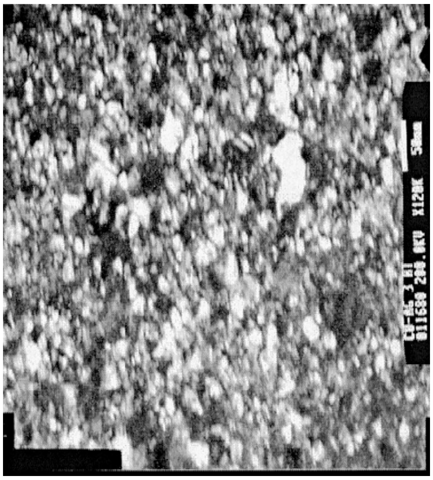

Fig. 3. Dark field TEM image after heat treatment (scale,—: 100 nm).

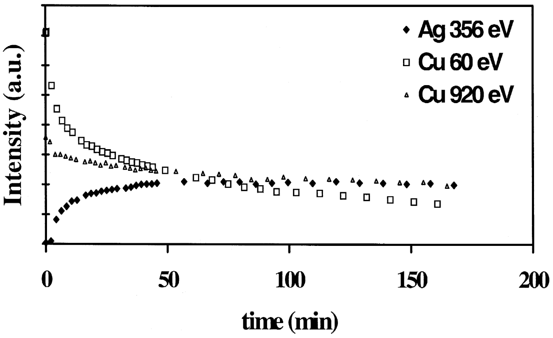

Fig. 4. Evolution of the Ag(356) and Cu(60–920) Auger peaks with time of heating at 428 K.

Taking into account that, in the left-hand side of Eq. (2), the c_s/c_0 ratio should be normalized between 0 and 1, the calculated c_s concentrations were normalized by this saturation value (i.e. is defined as unity). As it was mentioned in the theoretical part, for the evaluation of D_b a supposition on the δ/δ_s ratio is necessary. In Ref. [11], it was supposed that this ratio is about one. From elementary considerations, it would be expected that $\delta/\delta_s \leq 2$, if the structure of both the grain-boundary and the surface is determined by intrinsic factors only. Of course, if the surface is contaminated, this estimation cannot be valid. Thus, in the following, we will suppose that for one top layer limit $\delta/\delta_s = 2$, while for two monolayers $\delta/\delta_s = 1$ (since in this case the change in the surface structure is due to an extrinsic effect, i.e. due to the contamination).

Using Eq. (13) the relation between the accumulation factor q and the surface concentration c_s, as well as the Hwang–Balluffi equation with the sup-

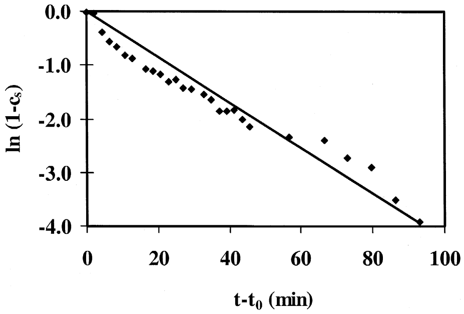

Fig. 5. The time evolution of c_s fitted by Eq. (13), $n = 1$.

Table 1
The obtained grain-boundary diffusion coefficients in the one- or two-layer limit (in Eq. (13), $n=1$ and $n=2$) at two temperatures

D_b [m^2/s]	413 K	428 K
In one-layer limit ($\delta/\delta_s=2$)	$2.10(\pm 0.16)\times 10^{-20}$	$4.66(\pm 0.18)\times 10^{-20}$
In two-layer limit ($\delta/\delta_s=1$)	$4.21(\pm 0.33)\times 10^{-20}$	$9.33(\pm 0.36)\times 10^{-20}$

posed conditions, the grain-boundary diffusion coefficients can be calculated (in the present experiment, $\lambda_{356}=5$, $\lambda_{920}=7$ [15], and $\omega=45°$). Results of D_b values calculated in one-layer limit ($\delta/\delta_s=2$) and in two-layers limit ($\delta/\delta_s=1$) are shown in Table 1. It can be seen that practically the results are different only because of the change of the δ/δ_s ratio.

The comparison of these values with the triple products ($kD_b\delta$) obtained for the grain-boundary tracer diffusion of Ag in Cu in B kinetics regime will be published in a next paper. As expected, a value larger than unity for the segregation factor (k) can be obtained. We will discuss in detail these results and the temperature dependence of k.

5. Conclusion

Surface accumulation method, called Hwang–Balluffi method [1], was applied to measure the grain-boundary diffusion of Ag at low temperatures (413 and 428 K) in a nanocrystalline Cu film. The rate of accumulation was detected by AES. The stability of the nanostructure was proved by TEM observations, and it was also shown that the results are not really sensitive to the supposition whether accumulation takes place in one or two monolayers of the surface (the results are different only because of the change of the δ/δ_s ratio).

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