DIFFUSION MECHANISMS IN THE Cu/Sb THIN FILM SYSTEM

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Résumé - L'interdiffusion dans les films minces bimétalliques de Cu/Sb est étudiée par rétrodiffusion Rutherford dans l'intervalle de température 150 - 300°C. Les profils de diffusion sont analysés à l'aide du modèle de Whipple. Les valeurs des coefficients de diffusion en volume de Sb dans Cu étant prises de la référence/12/, on trouve les énergies d'activation de diffusion par les joints de grains suivantes: 1,12 eV et 1,26 eV pour les échantillons respectivement, (600 Å Sb sur 650 Å Cu) et (1800 Å Sb sur 3100 Å Cu). Il est établi que les coefficients de diffusion par les joints de grains sont $10^3 - 10^6$ fois plus importants que ceux de la diffusion en volume extrapolés à partir des mesures de radiotraceur sur des échantillons massifs. Il est également observé que la diffusion est moins rapide dans les échantillons relativement épais.

Abstract - The interdiffusion of bimetallic Cu/Sb thin film couples is studied using Rutherford backscattering for annealing temperatures in the range 150 - 300°C. Depth profiles are analyzed using the Whipple's model. Taking the lattice diffusivities of Sb in Cu from Ref./12/, following activation energies for grain boundary diffusion are found: 1,12 eV and 1,26 eV for respectively (600 Å Sb on 650 Å Cu) and (1800 Å Sb on 3100 Å Cu) samples. It is established that the grain boundary diffusivities are 3 - 6 times larger than the lattice diffusivities predicted by an extrapolation of radioactive tracer measurements of bulk specimens. It is also observed that diffusion is lower in relatively thick samples.

1 - INTRODUCTION

Interdiffusion in thin film couples has attracted considerable attention because of the importance of thin films in microelectronic devices /1 - 3/. Understanding the diffusion processes is also very important in such areas of investigation as crystallization, precipitation, oxydation and surface segregation in alloys etc. It is known that diffusion occurs much faster in thin solid films than in bulk materials since the presence of point and line defects, grain boundaries and strains can enhance the diffusion processes. It is for this reason that diffusion in thin films can be observed at temperatures well below those at which equilibrium vacancies diffusion is negligible. Other factors which can influence the diffusion in thin films are detailed by Weaver /4/ and Balluffi and Blakely /5/. Diffusion measurements with thin films require high depth resolution due to the small film thickness and relatively short diffusion lengths at the temperatures of interest. Generally, analytical techniques such as Auger electron spectroscopy (AES) /6/, secondary ion mass spectrometry (SIMS) /7/ and Rutherford backscattering spectroscopy (RBS) /8,9/ are applied to such studies.

The objective of this study is to determine grain boundary diffusion parameters in Cu/Sb thin films using the RBS technique.

2 - EXPERIMENTAL PROCEDURE

The thin film couples are prepared by thermal evaporation in vacuum (10^{-6} Torr) of pure (99,99 %) Cu and Sb metals. Copper films are deposited onto glass substrates at 350°C and

then antimony films are deposited onto copper at 60°C. The two evaporation have been performed without breaking the vacuum. Two sets of samples are evaporated : (600 Å Sb on 650 Å Cu) for the first set and (1800 Å Sb on 3100 Å Cu) for the second. The film couples are annealed at 150 - 300°C in vacuum ($5 \cdot 10^{-6}$ Torr).

Analysis of the samples was performed with Rutherford backscattering spectrometry. In the experiment, He^+ ions with energy 1,4 MeV collimating through a slit system are allowed to hit normally the specimen surface. The detector forms an angle of 170° with respect to the incident direction. The detector signals are converted into an energy spectrum of the back-scattered ions. The concentration profiles are computed from the energy spectra.

Grain size measurements and electron diffraction patterns are obtained using a 200 keV transmission electron microscope and have been described elsewhere /10/.

3 - EXPERIMENTAL RESULTS AND DISCUSSION

Antimony diffusion in single-crystal copper was studied by the radioactive-tracer technique /11 - 13/. However in thin solid films, only one study has been realized using x-ray diffraction/10/.

Figure 1 shows energy backscattering spectra obtained from double layer films of 1800 Å Sb and 3100 Å Cu before and after annealing at various temperatures. The salient feature of this figure is immediately obvious from inspection of the spectra. There is no interdiffusion between the Sb and Cu films in an unannealed state, since the corresponding spectrum (Fig.1(1)) consists of two very distinct parts : the Sb spectrum on the higher-energy side and the Cu one in the lower-energy side. Annealing of samples at temperatures from 150 to 300°C increases significantly the interdiffusion (Fig.1 (2,3,4) for example).

Fig.1 - Rutherford backscattering energy spectra from 1800 Å Sb on 3100 Å Cu samples subjected to various stages of annealing : (1) as-evaporated, (2) after 230 min at 150°C, (3) after 195 min at 200°C and (4) after 130 min at 250°C.

In order to examine the diffusion of Sb in Cu thin films, we have used spectra such as those in fig. 1 to construct the diffusion profiles. Some of the depth profiles for the second set of samples before and after annealing are shown in Fig. 2. Profile broadenings at the interfaces due to diffusion are clearly evident. In many cases, long diffusion "tails" of nearly

constant concentration of Sb into the Cu underlayers are observed. These "tails" are related to grain boundary diffusion.

Fig. 2 - Diffusion profiles for Sb in Cu thin films from the data of Fig. 1.

Interdiffusion in thin films has most readily been understood in terms of Whipple's theory of diffusion /14/, in which grain boundary diffusion is separated from bulk diffusion. The grain boundary diffusion parameters can be determined by using Whipple's solution of the grain boundary problem with semi-infinite solid boundary conditions, assuming that the diffusion coefficients are independent of concentration and that diffusion in the grain boundaries (D_b) is much faster than direct diffusion through the grain (D_1).

According to Le Claire /15/, grain boundary diffusivities, D_b , can be calculated from the following equation :

$$\delta D_b = 0,66 \left(\frac{\partial \ln \bar{C}}{\partial z^{6/5}} \right)^{-5/3} \left(4 D_1 / t \right)^{1/2}$$

where $\bar{C}$ is the Sb concentration averaged at the depth of z from the original Cu/Sb interface, t is the diffusion annealing time and δ is the grain boundary width. This equation shows that a plot of $\ln \bar{C}$ as a function of $z^{6/5}$ is a straight line whose slope determines δD_b . we confine ourselves on the data for Sb diffusing into the Cu underlayer, i.e, the Cu side of the depth profiles. Some typical plots of $\ln \bar{C}$ versus $z^{6/5}$ are shown in Fig. 3.

δD_b can then be obtained from the slopes of "Whipple" plots taken in the diffusion "tail" region. The calculated values of D_b at various temperatures, taking the bulk diffusivities obtained at higher temperatures from /12/ and extrapolated to our temperature range and assuming δ of 10 Å, are presented in table 1 and shown in Fig. 4. If we assume an Arrhenius temperature dependence, the grain boundary activation energies are : 1,12 eV for 600 Å Sb on 650 Å Cu samples and 1,26 eV for 1800 Å Sb on 3100 Å Cu specimens.

According to the Cu/Sb equilibrium phase diagram /16/, there are two stable intermetallic compounds (Cu_2Sb and Cu_9Sb_2) in the considered temperature range. The solid solubility of Sb in Cu is about 3 at% at 300°C and 1,5 at% at 250°C. The grain boundary diffusion coefficients of Sb in Cu are determined for short periods of heat treatment such that the solid reaction between the two previous metallic films did not occur. Indeed, it has been found that, depending of the annealing temperature, the reaction was clearly produced after a certain annealing time of samples. To get an idea, the reaction was observed after about

10 min of annealing at 300°C of 600 Å Sb on 650 Å Cu sample, yielding to the formation and growth of the Cu₂Sb phase /17/. Therefore, the decrease (respectively increase) of Sb concentration in the Sb (respectively Cu) film, (Fig. 2, plateau of profile 4), could be attributed to the Cu₂Sb phase formation.

It is worth noting that the grain boundary diffusivities values measured here for Sb diffusion in Cu thin films are 3 - 6 times larger than the lattice diffusivities predicted from bulk measurements. The activation energies for the grain boundary diffusion in thin films are substantially lower than that for the volume diffusion (1,9 eV). This result confirms that thermal processes in thin films require temperatures lower than those necessary for the same reaction in a bulk sample, suggesting a grain boundary diffusion mechanism as the dominant process.

Fig. 3 - Whipple plot $\ln \bar{C}$ versus $z^{6/5}$ for 600 Å Sb on 650 Å Cu samples : (1) as-deposited, (2) annealed at 250°C for 10 min and (3) 300°C for 5 min.

Table 1. Grain boundary diffusion parameters of Sb in Cu thin films

Sample	Temperature (°C)	D_b (cm ² /s)	D_b^0 (cm ² /s)	E_b (eV)
First set d(Cu) = 650 Å d(Sb) = 600 Å	150	$3,66 \cdot 10^{-17}$	$7,46 \cdot 10^{-4}$	$1,12 \pm 0,01$
	200	$8,36 \cdot 10^{-16}$		
	250	$1,16 \cdot 10^{-14}$		
	300	$1,01 \cdot 10^{-13}$		

Second set	150	$3,25 \cdot 10^{-18}$		
$d(\text{Cu}) = 3100 \text{ \AA}$	200	$1,22 \cdot 10^{-16}$	$3,01 \cdot 10^{-3}$	$1,26 \pm 0,04$
$d(\text{Sb}) = 1800 \text{ \AA}$	250	$1,66 \cdot 10^{-15}$		
	300	$2,74 \cdot 10^{-14}$

Fig. 4 - An Arrhenius plot of the measured D_b values for Sb diffusion in Cu thin films: (1) first set and (2) second set of samples.

It is also observed that the diffusion in thinner samples (the first set) occurs more rapidly than in the relatively thicker samples (the second set). Indeed, the grain boundary diffusivities in the first case are about one order of magnitude larger and the activation energy is lower than the one in the second case. This feature is probably due to the grain structure of the films. The as-deposited Cu grains have an average grain size of about 1000 Å and 3000 Å respectively for the first and the second set of samples. On annealing, no significant grain growth is remarked.

It is interesting to underline that the value (1,26 eV) of the grain boundary activation energy for the second set of samples, is in agreement with the value (1,28 eV) found from X-ray diffraction measurements on (2000 Å Sb evaporated on 2700 Å Cu) samples /10/. The analysis technique used in /10/ did not distinguish between grain boundary and lattice diffusion, however, it is believed that the activation energy represents the grain boundary diffusion.

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