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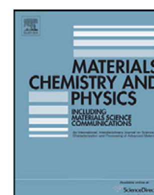

Phase formation of $Al_{10}Cu_{10}Fe$ in thin films

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ABSTRACT

This work deals with the investigation of the phase formation in thin film systems corresponding to the $Al_{10}Cu_{10}Fe$ phase composition. The samples were prepared by sputtering at room temperature. They were subsequently characterized using in situ resistance measurements, and in situ X-ray diffraction measurements from room temperature up to 600 °C. The first reaction occurs at the Al/Cu interface. The iron starts to take part into the phase formation for temperatures higher than 400 °C. At the end of the heat treatment, the sample is constituted of $Al_{10}Cu_{10}Fe$, only. This result is in agreement with the stable phase at the temperature of interest corresponding to the nominal composition of the sample.

The activation energy of the phase formation of $Al_{10}Cu_{10}Fe$ was determined from the in situ resistance measurements both by using simulation and Kissinger's method. Resistivity value of the $Al_{10}Cu_{10}Fe$ phase was also determined at room temperature.

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1. Introduction

The phase formation in the Al–Cu–Fe thin films systems have already been studied by several authors [1–7]. However all these studies focused on the same ternary composition which corresponds to the icosahedral phase i-$Al_{62.5}Cu_{25}Fe_{12.5}$. The interest in this phase lies on its exceptional properties: a very low electrical conductivity at room temperature, a surprisingly low thermal conductivity, a high hardness comparable to that of high strength steels, a low surface energy and a low friction coefficient [8–10]. The Al–Cu–Fe phase diagram shows three additional ternary phases (α, ω, φ) [11] and it was suggested that these additional ternary phases could also have potential applications such as for coatings or thermoelectric materials [12–13]. Eight ternary solid solutions based on binary phases (λ-$FeAl_3$, μ-Fe_2Al_5, υ-$FeAl_2$, β-AlFe, (Al), θ-Al_2Cu, η-AlCu, ζ-Al_3Cu_4, δ-Al_2Cu_3) were also reported in the sub-solidus projection of the ternary Al–Cu–Fe diagram proposed by Faudot [11]. The phase formation of α and ω in thin films was already studied by the authors [14]. The aim of the present work was to investigate the phase formation of the less well-known ternary phase, φ-$Al_{10}Cu_{10}Fe$. As far as we know, only Zhang et al. [15] investigated this phase. These authors found that it crystallizes in the *Fmm*2 (42) space group and that it is stable from room temperature up to 640 °C. No investigation of the phase formation in thin films has been reported yet for this phase.

Thin films of the constitutive elements of the phase were deposited with a sputtering set-up and the phase formation was studied during heating by using in situ resistance measurements and in situ X-ray diffraction (XRD) measurements. Simulations of the experimental results based on a theoretical model (see below) were also performed to get kinetic data on this phase formation.

2. Experimental and simulation procedures

2.1. Sample preparation and characterization

The thin films were fabricated in a multi-target sputtering deposition system. The vacuum pressure was around 10^{-7} mbar. The deposition was carried out under argon with a constant pressure of 1. 10^{-3} mbar. Layers of iron, copper and aluminum elements were sequentially deposited at room temperature on oxidized silicon wafers; the corresponding sequence is SiO_2/Fe/Cu/Al.

The wafer was rotating during deposition to improve the homogeneity of the layer. The thicknesses of the Al, Cu, and Fe layers were 112 nm, 80 nm, and 8 nm, respectively. The total thickness of the samples was then 200 nm. Thicknesses were checked using X-ray reflectivity technique.

In situ X-ray diffraction (XRD) measurements were performed with the Bragg-Brentano configuration using the Cu K_α radiation. The samples were loaded into XRD chambers, equipped with a heating stage in a vacuum of about 10^{-5} mbar. Two kinds of XRD chambers were used: a "low temperature chamber" in which measurements were performed each 10 °C from room temperature up to 400 °C, and a "high temperature chamber" for measurements from 150° to 600 °C. In the latter case, the XRD patterns were recorded each 10 °C. The heating rate between two scans was

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$5\,^{\circ}C\,min^{-1}$ in both cases. The diffractograms were recorded in the [15–55°] 2θ range, with a step size of 0.01° and a step time of 30 s.

Resistance measurements (Rs) were performed up to 600 °C in high vacuum conditions (10^{-6} mbar) by the four-point-probe method. Several heating rates ($1\,^{\circ}C\,min^{-1}$, $10\,^{\circ}C\,min^{-1}$ and $25\,^{\circ}C\,min^{-1}$) were used in order to determine the activation energy of formation of $Al_{10}Cu_{10}Fe$ by using the Kissinger method. Additional resistance measurements were performed on the sample after cooling in order to get the resistivity of the phase of interest at room temperature.

2.2. Simulation details

The simulations were carried out by using a program developed under MATLAB by one of the authors (D. Mangelinck). This program is based on the theoretical model presented in [16] which takes into account numerous physical parameters such as atomic volumes, coefficients of diffusion, energy of activation and thicknesses of the various layers.

The simulations were performed on the in situ resistance curves. Because of the complexity of the analysis, only the diffusion process was considered, whereas the interfacial reaction was neglected.

The evolution with respect to time of the thickness of the phases which are formed is given by the following equations:

$$\frac{de}{dt} = \frac{\alpha}{e} \qquad (1)$$

With $\alpha = K_d \frac{E_a}{K_B T}$

K_d is expressed according to:

$$K_d = K_{d0}\ \exp\left(-\frac{E_a}{K_B T}\right) \qquad (2)$$

where E_a is the activation energy for the diffusion process and K_{d0} is the growth rate.

3. Results and discussion

3.1. Experimental results

3.1.1. In situ X-ray diffraction measurements

The in situ XRD diffractograms recorded using the “low temperature chamber”, are presented in Fig. 1. The first phase is formed at around 130 °C, and it corresponds to Al_2Cu. The aluminum is entirely consumed by the reaction of formation of this phase. At around 170 °C, a new phase Al_4Cu_9 appears whereas the remaining part of Cu is consumed. Then Al_2Cu and Al_4Cu_9 react together at about 230 °C to form AlCu. At the end of the heat treatment, for temperatures around 400 °C, Al_3Cu_4 and β-AlFe are evidenced. AlCu is still present at these temperatures. The Al_3Cu_4 phase was identified by using the X-ray diffraction pattern reported by Gulay and Harbrecht [17].

The investigation of the phase formation was extended to higher temperatures by using the “high temperature chamber”. The corresponding diffractograms are plotted in Fig. 2.

In the overlapping range of temperatures of the chambers, the sequences of phase formation evidenced in the two chambers are identical. The phases which are formed are the following ones: Al_2Cu, Al_4Cu_9, AlCu and, Al_3Cu_4 with β-AlFe.

At around 480 °C, AlCu, Al_3Cu_4 and β-AlFe react together to form φ-$Al_{10}Cu_{10}Fe$ (see Fig. 2).

The reaction schema is presented in Fig. 3.

3.1.2. Resistance measurements

3.1.2.1. Resistance versus temperature. The evolution of the resistance with respect to temperature is presented in Fig. 4a for a thin film system corresponding to the φ-$Al_{10}Cu_{10}Fe$ composition. Generally speaking, a change of the slope on the resistance curve reveals a phase formation. In order to interpret these changes, four additional in situ resistance measurements were performed. In each of these measurements, the sample was heated up to a maximum temperature and “quenched” from this temperature down to room temperature by stopping the heating. The quenching temperatures are depicted by vertical lines in Fig. 4a. The obtained samples were then analyzed by XRD. The corresponding diffractograms are plotted in Fig. 4b. The diffractogram recorded at room temperature on the thin film system before heating is also presented in this figure. At 250 °C, the sample is constituted of AlCu and Fe. At 425 °C, one can see AlCu, Al_3Cu_4 and β-AlFe. At 475 °C and 560 °C, only $Al_{10}Cu_{10}Fe$ is observed. These results are in quite good agreement with those obtained by in situ X-ray diffraction. Therefore, the first phenomenon observed on the resistance curve (Fig. 4a) corresponds to the formation of Al_2Cu, Al_4Cu_9 and AlCu. The second one corresponds to the formation of Al_3Cu_4 and β-AlFe, and the last one to the formation of $Al_{10}Cu_{10}Fe$.

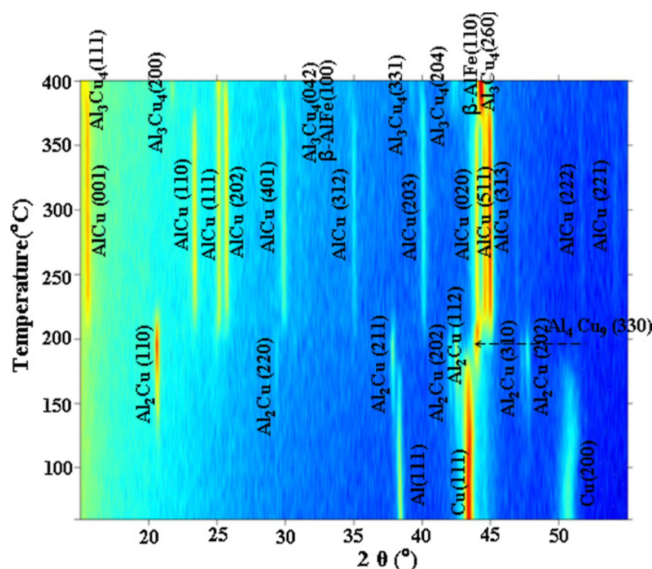

Fig. 1. In situ X-ray diffractograms versus temperature, obtained with the “low temperature chamber” for a thin film system corresponding to the φ-$Al_{10}Cu_{10}Fe$ composition.

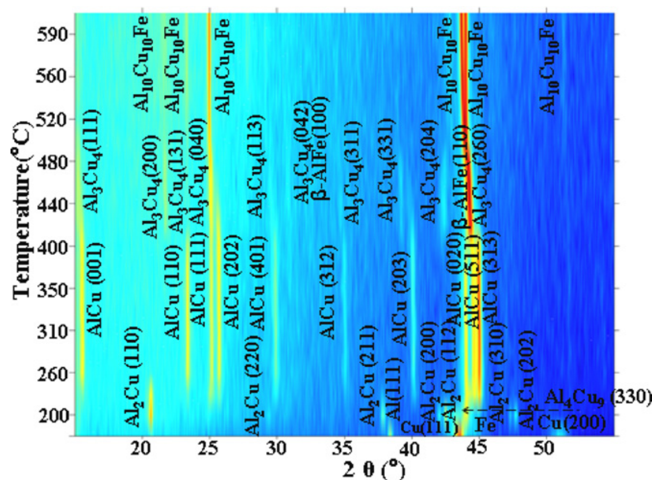

Fig. 2. In situ X-ray diffractograms versus temperature, obtained with the “high temperature chamber” for a thin film system corresponding to the φ-$Al_{10}Cu_{10}Fe$ composition.

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