Resistometric Evidence of Diffusional Mixing in Concentration Layered Amorphous AgCu Films

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In order to separate diffusion induced changes in the electrical resistivity of quench-condensed amorphous AgCu alloy films from such arising from other causes several trial experiments have been performed. Such films consisting of alternating $Ag_{60}Cu_{40}/Ag_{40}Cu_{60}$ layers showed a specific resistance rise which revealed the following peculiarities:

1. The duration of this increase is inversly proportional to the square of the individual $Ag_{60}Cu_{40}/Ag_{40}Cu_{60}$ couple thickness,
2. The increase is suppressed if rapid heating up to the crystallization temperature is performed and
3. It is not appearing in homogeneous layers.

These results give clear evidence that the observed effect is arising from diffusional intermixing only. Diffusion coefficients averaged over the annealing period are estimated as $D = 8.7 \times 10^{-15}\ cm^2\,s^{-1} \times \exp 0.89\ eV/kT$.

The electrical resistivity is a simple and attractive means to study local changes in concentration of inhomogeneous thin films whenever the concentration dependence of the resistivity is nonlinear and sufficiently pronounced [1–4]. However, in order to distinguish resistance changes due to the atomic transport from those resulting from structural relaxation, defect annealing, pick up and release of gaseous components [5] etc., additional experiments are necessary.

Like some other binary metallic systems [6], amorphous CuAg alloys show a parabolic dependence of the electrical resistivity on concentration [7]; thus observation of diffusional mixing processes in thin stratified layers should be possible (Figure 1).

Considering concentration modulated films, the initial resistance is given by the original laminae's average resistance whereas the resistance in the final state is that of the mixed homogeneous film. The latter is higher if the film concentrations lie on either side of the concentration for maximum resistivity (Figure 2).

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Sample Preparation

The amorphous CuAg films were evaporated at 10^{-7} Pa by quenching the mixed vapour onto LN_2-cooled substrates. A special masking system allowed for the deposition of concentration modulated films consisting of uniform layers A and B. The annealing

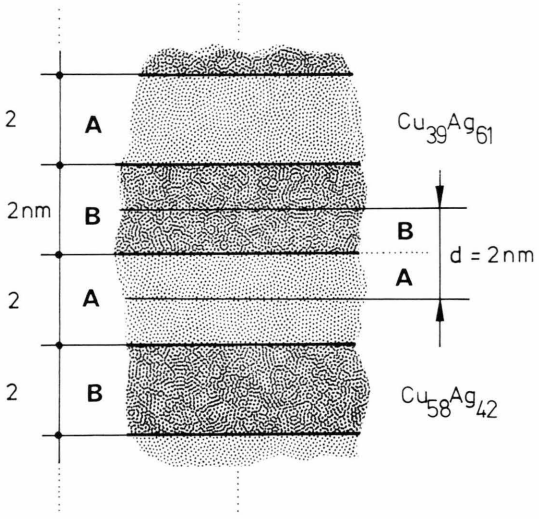

Fig. 1. Schematic diagram of a concentration modulated film; d is the diffusion length.

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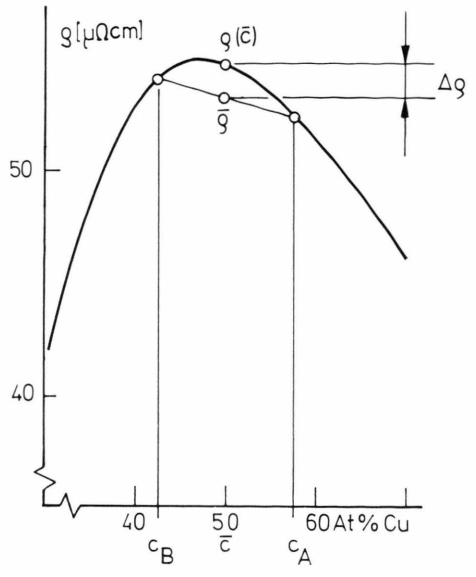

Fig. 2. Change in the resistivity of a stratified film due to diffusional mixing. The solid curve resembles the concentration dependence of the resistivity for amorphous CuAg films.

was performed immediately after deposition, first by linear heating, then isothermally at the temperature where the diffusion was to be studied. Other experimental details are found elsewhere [8].

Results

The annealing behaviour of the resistance of a modulated film is shown in Fig. 3 together with the annealing programme. The increase in resistivity, which is thought to be caused by the diffusional mixing, starts already at 250 K. After a certain time, the resistivity approaches a constant value indicating the end of the diffusion process. The diffusion time t_d is estimated form the inequality

$$t_{max} \geqq t_d \geqq t_{min} \tag{1}$$

(t_{min} is measured from the beginning of the isothermal anneal, whereas t_{max} is estimated from the begin of the resistivity increase; both time intervals end when the stabilization of the resisitivity is ob-

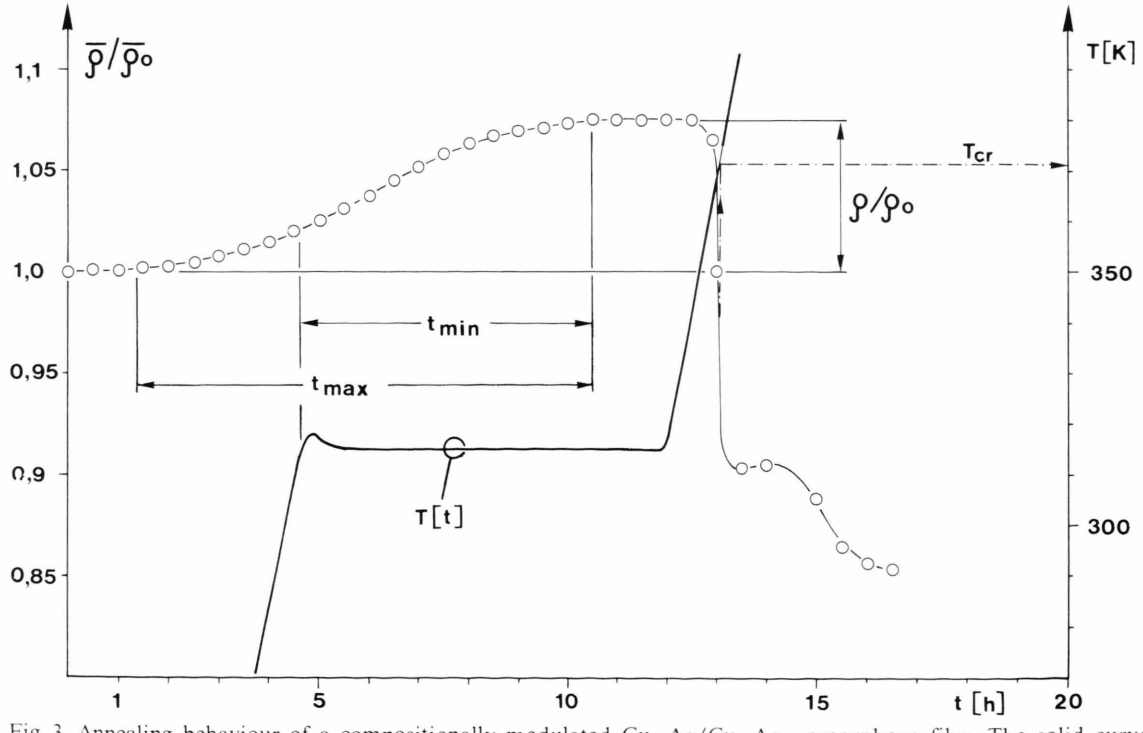

Fig. 3. Annealing behaviour of a compositionally modulated $Cu_{39}Ag/Cu_{58}Ag_{47}$ amorphous film. The solid curve $T(t)$ resembles the annealing programme.

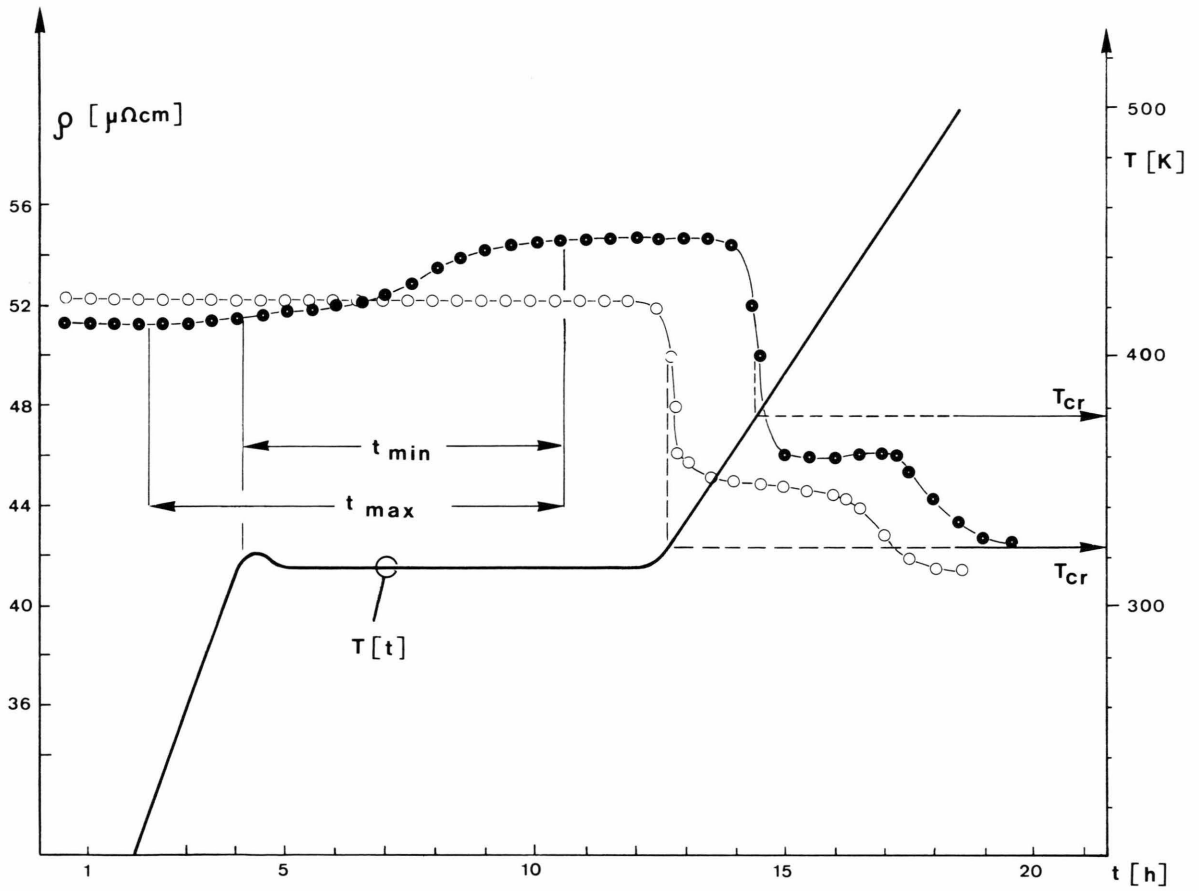

Fig. 4. Comparison between the annealing behaviour of the resistivity of a modulated film and that of a homogeneous one. ● concentration modulated film; ○ homogeneous film.

tained). The diffusion coefficient is then certainly found in the interval D_{max}, D_{min} defined by

$$D_{max} = d^2/t_{min}\,, \quad D_{min} = d^2/t_{max}\,. \tag{2}$$

To make sure that the increase of resistivity was due only to diffusional intermixing and not to any artifact or induced effect, the following experiments were carried out.

Comparison Between a Modulated and a Homogeneous Film

Two films were investigated simultaneously, one was modulated as described above whereas the other one was a homogeneous $Cu_{58}Ag_{42}$ film. For comparison their annealing behaviour is shown in Figure 4.

Only the modulated film exhibits an increase of the electrical resistivity. Crystallization of the still amorphous films can be triggered by a further temperature rise.

Like the electrical resistivity, the crystallization temperature shows a concentration dependence [8] with a maximum next to 50 at%. Hence, any change in the crystallization temperature gives evidence for a corresponding change in concentration. For 39 and 58 at% Cu, the crystallization temperatures are 344, 332 K respectively, whereas the originally modulated film crystallized at 371 K. This increase in the crystallization temperature can be interpreted only as a result of the interdiffusion process which homogenized the film.

In order to support this explanation, the above experiment was repeated with a continuous and

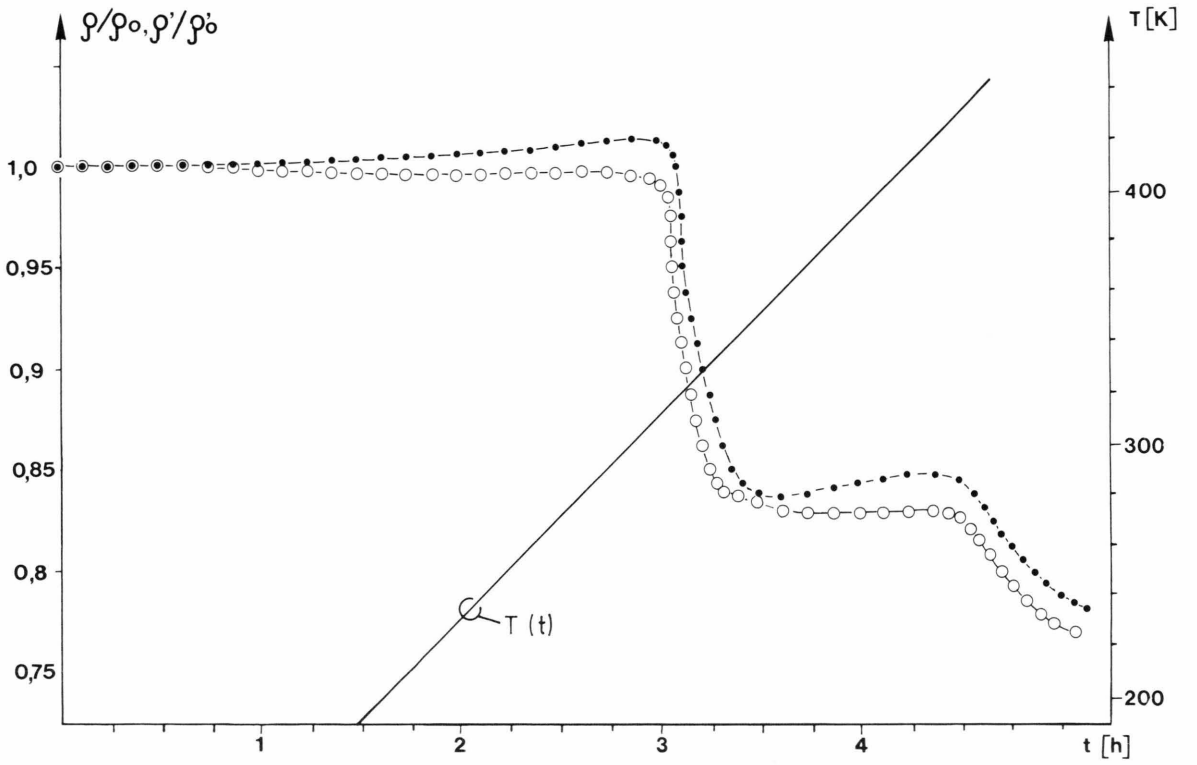

Fig. 5. Suppression of the diffusion process in a modulated film. ● concentration modulated film; ○ homogeneous film.

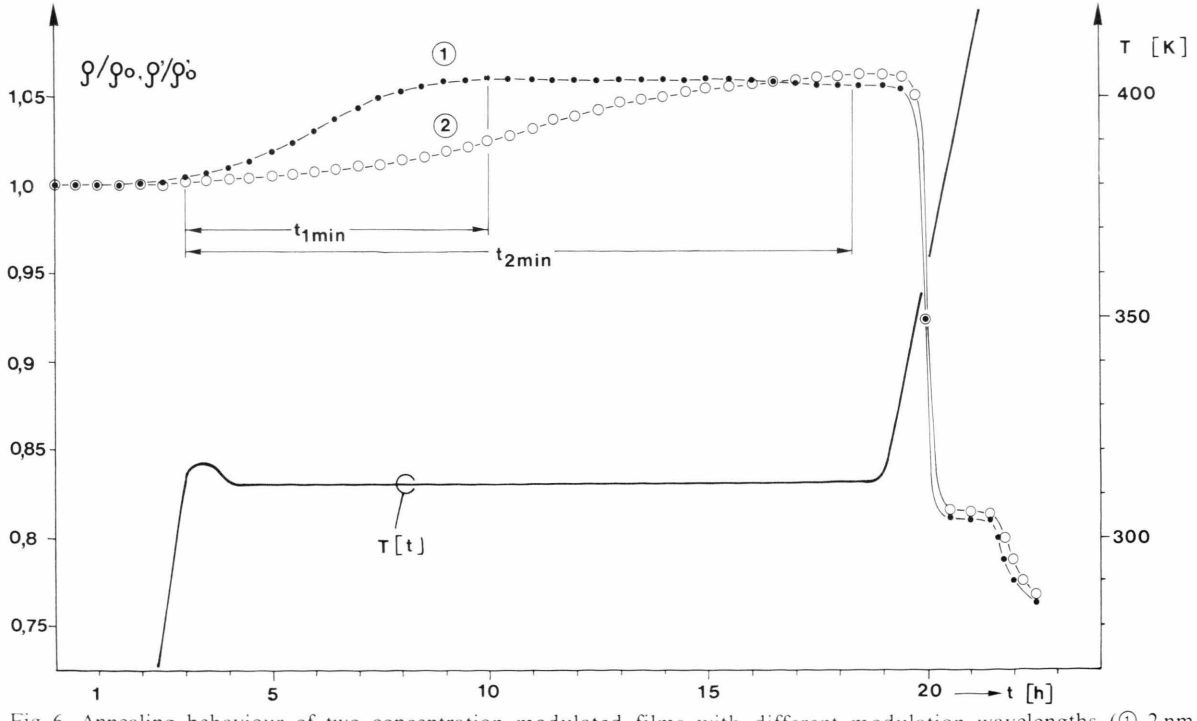

Fig. 6. Annealing behaviour of two concentration modulated films with different modulation wavelengths (① 2 nm, ② 3 nm).

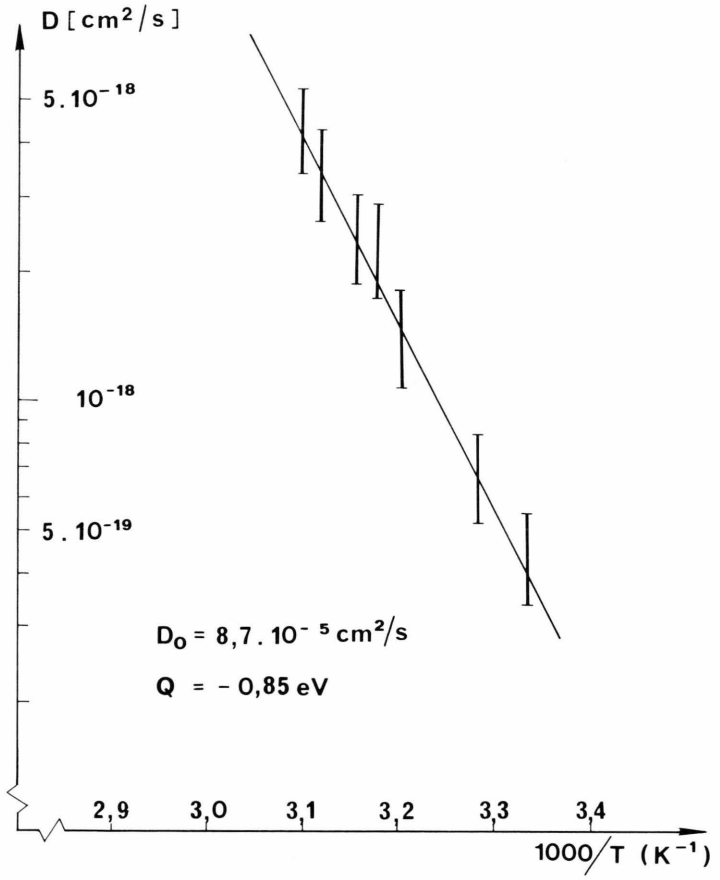

Fig. 7. Arrhenius plot of the mean diffusion coefficient in amorphous CuAg thin films.

rapid rise of the temperature in order not to allow the intermixing process to take place completely (Figure 5). As expected, only a very small increase in the resistivity of the modulated film was recorded in this case. Moreover, almost no increase in the crystallization temperature was detected. This experiment again gives support to conclude that the detected increase in the crystallization temperature and in the electrical resistivity is due to interdiffusion only.

Thickness Dependence of Diffusivity

A third criterion to check the above interpretation is the increase of the diffusion time with thickness. It was checked by annealing two modulated films of different modulation wavelength (2 and 3 nm respectively). The annealing behaviour of these films is displayed in Figure 6. Both films were annealed isothermally at 312 K. The diffusion times were 7 and 15.3 h respectively i.e. the relation

$$\frac{t_1}{t_2} = \left(\frac{d_1}{d_2}\right)^2 \tag{3}$$

is fairly fullfilled by the experiment revealing a ratio $t_1/t_2 = 0.46$.

Temperature Dependence of Diffusion

After such conclusive trial experiments the relations (2) can doubtlessly be applied to estimate the diffusion parameters. For different annealing temperatures the diffusion data are given in Table 1.

These values have to be considered as mean values irrespective of any possible changes in the diffusivity during the process itself. In another paper we deal with the actual instantaneous diffusivities and their change during the anneal. Such a treatment is based on a more detailed analysis of the annealing curves of the resistivity [9].

Table 1.

T	C_1	C_2	d	n	t_{min}	t_{max}	D
300	37	59	20	10	23	25	0.45
305	37	59	17	12	8.3	11	0.7
312	39	57	30	10	16.4	18	1.4
312	39	57	20	10	7.1	8.5	1.4
315	39	58	25	10	6.9	9	3.3
317	40	60	25	8	6.5	8	2.4
319	39	58	20	10	3.9	7.5	3.4
322.5	41	58	25	10	3.5	5.5	3.95

T	diffusion temperature	(K)
C_1, C_2	initial concentrations of the modulated films	(at% Cu)
d	thickness of the diffusion couple	(nm)
n	number of the diffusion couples	
t_{min}	minimum diffusion time, measured during the isothermal annealing	(h)
t_{max}	maximum diffusion time, measured from the beginning of the resistivity rise to its stabilization	(h)
D	mean diffusion coefficient	(10^{-18} cm^2 s^{-1})

The diffusivities obey an Arrhenius relation (Fig. 7) of the form

$$D = 8.7 \times 10^{-5} \exp(-0.85/kT)\ \text{cm}^2/\text{s},\ kT \text{ in eV}. \quad (3)$$

Conclusion

The anneal of concentration modulated thin amorphous AgCu films is associated with an increase of their resistivity. The change of the duration of the resistance rise with film thickness, the suppression of this increase by rapid heating to the crystallization temperature and the fact that in homogeneous films no resistance change is observed are convincing arguments for assigning the above effect to diffusional mixing.

Hence diffusion coefficients could be estimated from the resistance change of concentration modulated amorphous CuAg films during annealing.

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