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TRANSIENT INTERFACE SHARPENING IN MISCIBLE ALLOYS

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Abstract

Using computer simulations, it was shown [1, 2] that on the nanoscale, for strongly composition-dependent diffusion coefficients, an initially diffuse A/B interface can become chemically abrupt even in ideal systems with complete mutual solubility.

Our recent work [3] provides the first experimental evidence for the predicted interface sharpening. This is shown in situ, during heat-treatments at gradually increasing temperatures, by scattering of synchrotron radiation in coherent Mo/V multilayers containing initially diffuse interfaces.

Keywords: interfaces, diffusion in crystalline Mo/V, interface sharpening, simulation, experiment, synchrotron

1 Introduction

With still continuously shrinking device structures, the question of how the physics of atomic interdiffusion may change on the nanoscale appears of utmost importance. A possibly new behaviour could help to improve device properties or hinder its destruction.

Using computer simulations, it was recently shown [1, 2] that on nanoscale, for strongly composition-dependent diffusion coefficients, an initially diffuse A/B interface can become chemically abrupt even in ideal systems with complete mutual solubility. This sharpening is surprising at first sight because the macroscopic Fick I law states that the direction of diffusion is always opposite to the direction of the composition gradient.

This predicted behaviour is interesting not only from fundamental research point of view, but it is very promising in terms of applications as well. It could provide a useful tool for the improvement of interfaces and offer a way for fabrication of e.g. better X-ray or neutron mirrors, microelectronic devices or multilayers with giant magnetic resistance.

2 Theory

Using computer simulations, it was recently shown [1, 2] that on the nanoscale, for strongly composition-dependent diffusion coefficients, an initially diffuse A/B interface can become chemically abrupt even in ideal (either crystalline or amorphous) systems with complete mutual solubility. This sharpening is surprising at first sight because the direction of diffusion is always opposite to the direction of the composition gradient: $J = -D \, \mathrm{grad} \, c$, with J the atomic flux, D the diffusion coefficient and c the concentration. Indeed, for constant D, the composition profile will gradually decay and a flattening of the (sharp or diffuse) interface is expected. On the other hand, when the diffusion coefficient strongly depends on the local composition, the flux distribution can lead to a sharpening of the interface; see Fig. 1. The sharpening can be qualitatively predicted from the classical Fick I law although it is not able to provide correct kinetics on nanoscale [1, 4].

3 Experimental

We studied Mo/V multilayers [3]. The structures (20 bilayers with a modulation length ≈ 5-6 nm) were produced by magnetron sputtering. The pure Mo and V layers were separated by a roughly 1 nm thick diffuse interface with a constant composition gradient. In order to follow the change of the composition profiles in situ during heat treatments, x-ray measurements were

performed at the KMC2 beamline at the BESSY synchrotron, Berlin.
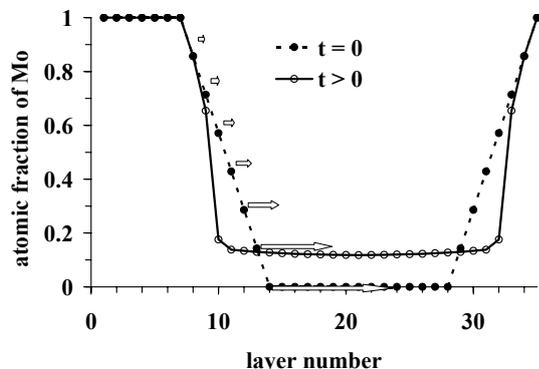
Figure 1: Composition distribution during intermixing in one period of a Mo/V multilayer calculated from an atomistic model, as in [1]. The arrows represent schematically the `flux distribution', i.e. their lengths are proportional to the absolute value of the atomic flux.

The samples were placed on a heater inside a hemispherical Be window under high-vacuum conditions. Measurements were carried out at temperatures that gradually increased from 293 K up to about 973 K in 10 steps. At each temperature consecutive symmetrical scans between 53° and 66° of the scattering angle 2Θ were performed, measuring the scattering intensity around the (002) Bragg reflection of the Mo/V multilayer structure. The sample was kept at a certain temperature until no change in the diffraction pattern could be observed, and this required a minimum of two hours.

The x-ray diffraction patterns were reconstructed using two models based on the works of Stearns [5] and Fullerton et al. [6]. However, the shapes shown in Fig. 1 for $t > 0$ cannot be handled in these models and we had to modify them [3].

4 Results

Figure 2 shows the diffraction patterns measured during heat treatment and their fits by the modified Stearns model. As can be seen, we could reproduce the measured diffraction patterns almost perfectly. Within the error limits both models gave the same layer and interface thicknesses, presented in Fig. 3.
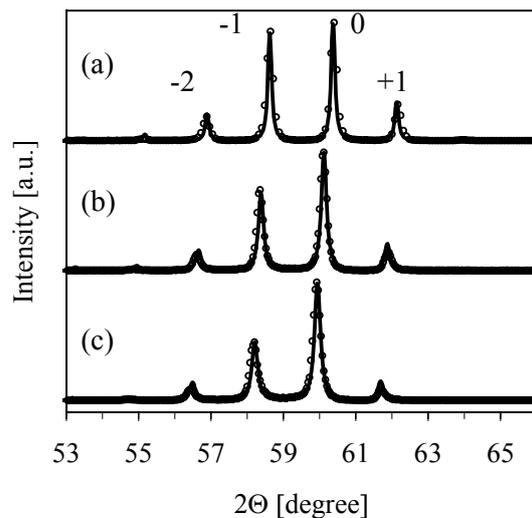
Figure 2: Diffraction patterns measured (circles) during the heat treatments and their reconstructions by the modified Stearns model (solid line): (a) room temperature, (b) 903 K, and (c) 953 K.
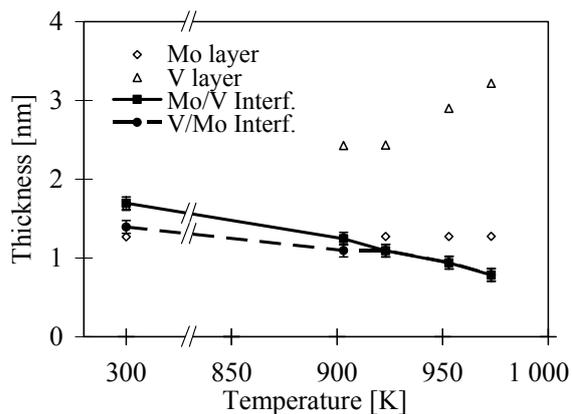
Figure 3: Thickness of the interfaces as well as the pure Mo and V layers, as obtained from the fits. Error bars show the estimated errors of fitting. In case of the pure Mo and V layer, respectively, error bars are comparable to the symbol sizes. The solid curves are to guide the eye.

We find that initially the Mo/V interfaces were slightly thicker than the V/Mo ones, and this difference decreased during sharpening. This observation is in accordance with the results obtained in Si/Ge [7], Co/Cu [8] and Au/Ni [9, 10] multilayers. During deposition of one element (e.g. A) having a segregation tendency on the surface of the other (B), a segregation-assisted

intermixing takes place and the B/A interface is more diffuse than the A/B one.

Since the fits resulted in a decreasing interface thickness, we conclude that the interface sharpened during the heat treatment.

Finally, the fact that at a fixed temperature no more changes were observed after a certain time, i.e. a gradually increasing temperature was necessary, also gives a proof of sharpening. Since the interface is sharper, the Mo atoms are bound more strongly in the interface (the interface is more and more Mo-rich), consequently their diffusion into the V is slower, see also Fig. 1. Thus, in order to counterbalance this effect, we had to increase the temperature slightly (the diffusivity has exponential dependence on both the temperature and the composition).

One may argue that other effects could perhaps produce a similar evolution. For example stress development and relaxation during intermixing could be one of the most relevant effects. However, as was shown in [2], the composition profile develops similarly as in stress free case (see also Fig. 4 and 5) only the timescale of the process is expected to change (see also Fig. 6).
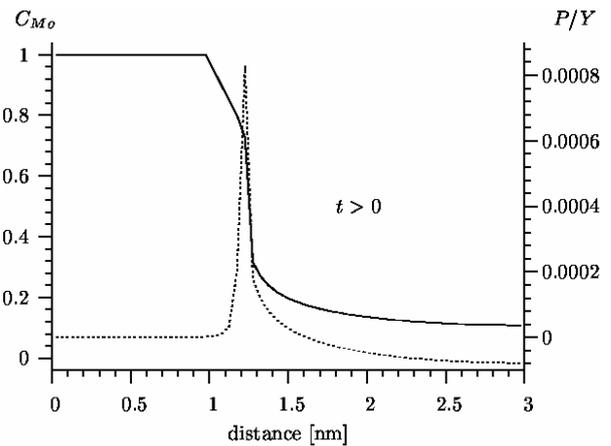
Figure 5: Time evolution of the composition profile of Mo at $t > 0$ when only the diffusional stress is taken into account (The initial state is the same as in Fig. 4a). The dotted line is the normalised pressure [P/Y where $Y = E/(1-\nu)$, E Young's modulus, ν Poisson's ratio] (see also Ref. [2])

Figure 4: Time evolution of the composition profile of Mo, at two different times, when all the stress effects are ignored. (see also Ref. [2])
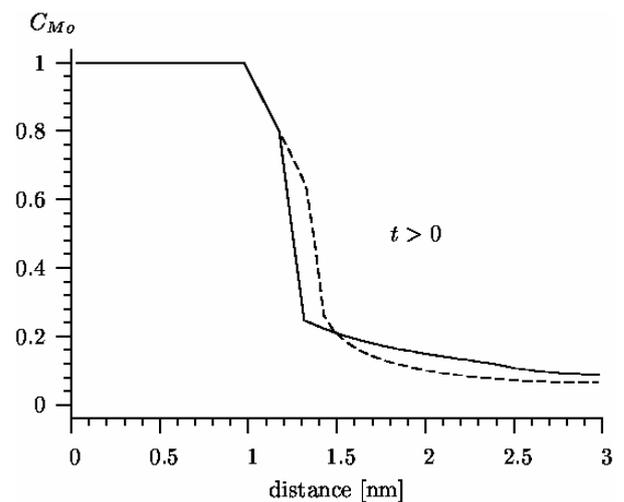
Figure 6: Demonstration of the influence of the `strength' of the diffusional stress: week stress − solid line, strong stress − dashed line. (see also Ref. [2])

5 Conclusions

In conclusion, we successfully followed in situ interface sharpening in coherent Mo/V multilayers. The thickness of the Mo layers did not change apart from a tiny increase caused by thermal expansion. In contrast, the V-rich layers became much thicker, which cannot be explained solely by thermal expansion. The interface thicknesses decreased by about a factor of two (from 1.7 and 1.4 nm, respectively, to 0.78 nm), confirming the sharpening effect.

Acknowledgments

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