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Interface kinetics and morphology on the nanoscale

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ABSTRACT

Diffusion on the nanoscale in multilayer, thin films has many challenging features even if the role of structural defects can be neglected and 'only' the effects related to the nanoscale arise. Recently, we have discovered different examples for diffusional nanoscale effects, which are summarized in this contribution. Interface shift kinetics may be different from the ones predicted by continuum approximations (anomalous kinetics). Moreover we show that in solid state reactions, reaction layers form and start to grow highly non-stoichiometrically and an initially existing stoichiometric compound layer may dissolve then re-form non-stoichiometrically. Our findings are of primary importance for nanotechnologies where early stages of solid state reaction (SSR) are utilized. We also show that an initially diffused interface may sharpen even in completely miscible systems. This phenomenon could provide a useful tool for the improvement of interfaces and offer a way to fabricate, for example, better X-ray or neutron mirrors, microelectronic devices, or, multilayers with giant magnetic resistance.

A variety of different UHV-based techniques (AES/XPS and synchrotron facilities) have been used to prove the above theoretical findings in different systems (e.g. Ni/Cu, Ni/Au, Si/Ge, Co/Si).

1. Introduction

In the last 5–10 years, we have been intensively working on computer simulations and experimental investigations of interface motion and transformation. With still continuously shrinking device structures, the question of how the microscopic laws may change on the nanoscale appears of utmost importance. This is not only interesting from a fundamental point of view but is also of practical interest. Planning and fabrication of nanoscale devices need better understanding of the atomic scale processes. Possible new behaviour could help to improve the properties of devices.

Different examples for diffusional nanoscale effects will be given in this contribution [1–5]. We will illustrate that interface shift kinetics may differ from the ones predicted by continuum approximations (anomalous kinetics). These findings led us to investigate solid state reaction kinetics. We will show that, in many realistic cases, reaction layers form and start to grow highly non-stoichiometrically. Moreover an initially existing stoichiometric compound layer may dissolve then re-form non-stoichiometrically [6]. We will also show that an initially diffused interface can sharpen even in completely miscible systems [7,8].

A variety of different UHV-based techniques have been used to prove the above theoretical findings. The interface shift kinetics has been measured by means of surface analytical techniques (AES, XPS) during dissolution of thin films into semi-infinite substrates: Ni/Cu(111), Ni/Au(111), Si/Ge(111), a-Si/a-Ge. Solid state reactions in the Co/Si system have been studied by synchrotron X-ray diffraction. Depth profiling was performed by Extended X-ray Absorption Fine Structure (EXAFS) analysis in a waveguide structure, which is a rather new method [9]. The interface sharpening has been measured by synchrotron X-ray diffraction [10].

2. Diffusion asymmetry – sharp interface shift

2.1. Computer simulations

To investigate the interface kinetics and morphology we used basically two types of models: continuum and discrete (atomistic). The advantage of the continuum models over atomistic ones is that stress effects can easily be included. However the validity of the continuum models is limited on the nanoscale, especially if the diffusion coefficient (D) is *composition dependent* [11]. For example $D = D_0 \exp(mc)$, where c is the atomic fraction and m measures the strength of the composition dependence of D. It is convenient to introduce an m' parameter instead of m, where $m' = m \log_{10}(e)$ and e is the base of the natural logarithm. m' gives, in orders of magnitude, the difference between the diffusion coefficients in the pure A and B matrixes (*diffusion asymmetry*). The range of the validity of the continuum model shifts strongly with increasing m'

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and, in many real thin- or multilayer systems with typical characteristic length of few nanometers, it may break down.

However, both from the discrete and continuum models, we obtained that the development of the composition profiles is quite symmetrical for composition independent D, whereas, for strong composition-dependent D (strong diffusion asymmetry), the composition profiles are very asymmetric. The interface between the A and B matrixes remains abrupt and shifts until the component in which the diffusion is slower is no longer consumed. It can be seen in Fig. 1 that the Si atoms diffuse very fast into the Ge matrix and are distributed homogeneously, whereas the Ge atoms practically cannot penetrate into the Si matrix, since the diffusion is more than 4 orders of magnitude faster in the Ge than in the Si [11].

The *discrete* model used in our calculations is a kinetic mean field (KMF) model based on Martin's equations [12]. However, we use our own composition-dependent activation energy barriers in the exchange frequencies, which unify the advantages of other barriers used in the literature as we have shown earlier [13].

Another atomistic computer simulation we used is the kinetic Monte Carlo (KMC) method. In our KMC, to calculate the jump probabilities, we also used the improved form of the activation energies mentioned in Ref. [13].

2.2. Experiments

Amorphous Si/Ge multilayers with nearly equal thickness of sublayers were prepared by dc magnetron sputtering. The nominal thickness of the Si and Ge sublayers was 18 nm, the total thickness of the multilayer was 180 nm. The asymmetric development of the composition profile was shown by measurement of the time evolution of the composition profile by the Auger depth profiling technique. It was shown that, during annealing, the Si atoms diffuse into the Ge and are homogenised there. As a consequence, the interface shifts towards the Si resulting in the thinning of the Si layer and thickening of the initial Ge layer, within which, the Si content increases (Fig. 2) [14].

3. Anomalous (non-Fickian) interface shift kinetics

It is known from Fick's phenomenological laws that, during annealing of a diffusion couple, the displacement of a plane with constant composition (or an abrupt interface) is proportional to $t^{1/2}$ (Fickian or normal shift kinetics with t equal to time). However, as was shown above the validity of Fick's laws is limited on the nanoscale, especially with increasing diffusion asymmetry. Therefore, we revisited the problem of the interface shift kinetics on the nanoscale.

In order that we could systematically study the interface shift kinetics, we divided the problem into two parts. First we studied the completely miscible ($V = 0$, where V is a solid solution parameter proportional to the mixing energy of the system) and phase separating ($V > 0$) systems. In these cases only the shift of one interface is to be studied. Second, we investigated ordering systems, where the kinetics of two interfaces is to be followed since a growing new AB ordered phase connects to both the pure A and B matrixes ($A/AB/B$).

3.1. Completely miscible ($V = 0$) and phase separating ($V > 0$) systems

3.1.1. Computer simulation and theory

To investigate the interface shift, we recorded sequentially the position of the interface of a diffusion couple [2]. Its logarithm versus the logarithm of the time ($\log p \propto \log t$) was plotted. Fitting a straight line to the data, its slope gave the power of the function describing the shift of the interface (called *kinetic exponent* and denoted by k_c). Obviously for parabolic interface shift $k_c = 0.5$. Thus if the kinetics is non-Fickian, $k_c \neq 0.5$ or the data do not fit on a straight line on the $\log p \propto \log t$ plot. Both the parameters m' and V (or V/kT) were changed during the calculations.

Fig. 3 shows the initial values of k_c versus V/kT for different m' values. It can be seen that k_c is almost constant and, as expected, is very close to 0.5 for small m'. At the same time, the deviation from the square-root kinetics increases with increasing m' for a fixed value of V/kT.

The deviation from the parabolic law is a real "nano-effect" because, after dissolving a certain number of layers (long time or macroscopic limit), the interface shift returns to the parabolic behaviour independently of the input parameters.

We have shown [5], that this transition can be understood from the analysis of the atomic currents in the different parts of the sample. In principle three currents can be distinguished: i) J_α in matrix A, where the diffusion is very slow, ii) J_I across the interface region and iii) J_β in matrix B, where the diffusion is fast (see Fig. 4). However, J_α can be neglected, because, practically, there is no diffusion in matrix A. Moreover, at the beginning of the kinetics, when the composition gradient is very large, the flux in the B-rich phase (β phase) is larger than across the interface ($J_I < J_\beta$). In this stage J_I controls the diffusion. During the process J_β becomes smaller and smaller because the tail of the composition profile in

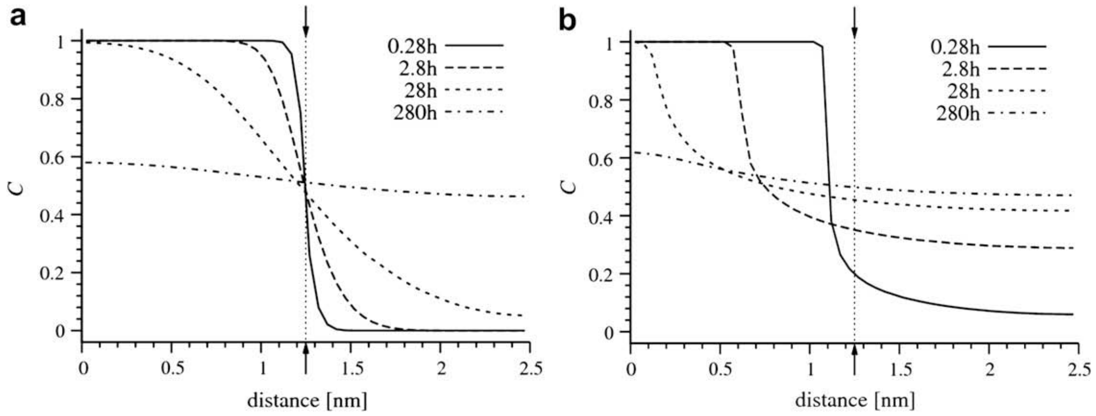

Fig. 1. Concentration distributions of Si in a Si/Ge multilayer (only half bilayers are shown for symmetry reasons) at different times for the continuum model. (a) Composition independent D, i.e. $m' = 0$ (b) composition-dependent D, where $m' = 4$. The arrows show the initial position of the interface.