diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Anomalous Diffusion on the Nanoscale in Binary Alloys

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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 fundamental point of view but also of practical interest. To plan and fabricate nanoscale devices need better understanding of the atomic scale processes. A possibly new behaviour could help to improve the properties of devices or hinder their destruction.

Diffusion on the nano/atomic scales in multilayers, thin films has many challenging features even if the role of structural defects can be neglected and 'only' the effects related to the nano/atomic scale raise. Different examples for diffusional nanoscale effects, we have discovered recently, will be given in this contribution. We show that the continuum descriptions of the diffusion cannot be applied automatically on such short distances, the classical continuum approximations (Fick's laws) cannot describe correctly the atomic movements. [1-3]. They predict faster kinetics than the atomistic models and the interface shift is always proportional to the square-root of the time ($x \propto t^{1/2}$: classical or Fickian kinetics). As we will illustrate, however, the kinetics can be even linear ($x \propto t^{k_c}$ where $0.25 \le k_c \le 1$) on the nano/atomic scale. [1-4] Furthermore, the continuum descriptions foretell infinitely fast kinetics as the time goes to zero ($v = \mathrm{d}x/\mathrm{d}t \propto 1/t^{1/2}$), which is a long standing paradox of the diffusion theory. We will present a possible resolution of this paradox. [5] Moreover, we will show that an initially diffused interface can sharpen even in completely miscible systems. [6, 7]

2. Anomalous interface shift

It is known form 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 $t^{1/2}$. However, we have shown first from computer simulations that this rule can be violated on the nanoscale either in completely [1] or restrictedly miscible systems [2]. This is strongly related to the discrete character of the system on the nanoscale and to the highly neglected fact in the literature that the diffusion coefficients or mobilities depend on the composition. However, this anomaly is restricted only to short length / time scales, on the microscopic scale the kinetics returns to the classical square-root time scale independently of the input parameters. We have shown very recently [5], that this transition can be understood from the analysis of the atomic currents in the vicinity of the interface. Moreover, from the analysis of the currents an atomistic explanation of the phenomenological interface transfer coefficient can also be given, which has been missing in the literature on reaction diffusion.

We have also measured the anomalous interface shift both in completely miscible (Ni/Cu) [1] and restrictedly miscible (Ni/Au) [3] *crystalline* systems. Moreover, recently we have also observed it in an *amorphous* Si/Ge system. What is more, in this system we have managed to observe the anomalous – classical transition of the kinetics. [4]

3. Interface sharpening in completely miscible alloys

Computer simulations also have shown that on the nanoscale, for strongly composition-dependent diffusion coefficients, diffuse interfaces can sharpen rather broaden in completely miscible binary systems during annealing [6-7]. Later on, we have managed to observe the sharpening in epitaxial Mo/V multilayers [8]. This sharpening is surprising at first sight, because the direction of diffusion is always opposite to the direction of the composition gradient. This phenomenon could provide a useful tool for the improvement of interfaces and offer a way to fabricate e.g. better X-ray or neutron mirrors, microelectronic devices or multilayers with giant magnetic resistance.

4. Conclusions

We have shown from computer simulations that Fick's laws are violated on the nanoscale either in completely or restricted miscible systems. This is strongly related to the discrete character of the system on the nanoscale and to the highly neglected fact in the literature that the diffusion coefficients or mobilities depend on the composition. Computer simulations also have shown that on the nanoscale, for strongly composition-dependent diffusion coefficients, diffuse interfaces can sharpen rather than broaden in completely miscible binary systems during annealing. These phenomena predicted by computer simulations have been proved experimentally as well.

Acknowledgements

This work was supported by OTKA grants K61253. Z. Erdélyi acknowledges support from Bolyai János Foundation.

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