



Relationship between solid state diffusion and mechanical stresses

Thesis of (PhD) doctorate

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Introduction

The research of diffusion phenomena grew to huge dimension in the last century. Scientists were interested in this topic earlier, but the appeared questions were related to the diffusion phenomena, which took place rapidly at room temperature, eg: diffusion of gases and fluids.

Ernest Kirkendall carried out one of the base experiments of solid-state diffusion in the first half of last century (1947). The corollary of his experiment changed the idea of solid-state diffusion: the diffusion can also take place by vacancy mechanism.

The solid state diffusion and reaction are important phenomena in much area of the technology. The processes - induced by diffusion – influence the large scale of materials, eg: composit materials, preparation of welded components, coating, production of multi layered microelectronic devices.

Investigations of this topic established the relation between the diffusion as a basic phenomenon and the industrial applications in large scale. Revolutionary development of computer technology begun in that years, which involved the development of faster, smaller and higher capacity hardware. High precision in control of diffusion process is needed at this level of micro technology.

The study of bilayer's behaviour during annealing is needed by technological development, eg: metallization of **Si** integrated circuits. The **Cu** and **Al** are widespread such as metal wires in ICs and external contact. Beside electron migration the **Al**, **Cu** go into the **Si** and can ruin the contact. To avoid this case the **Al**, **Cu** should be separated from the **Si** by an energy barrier, it consist of transition metals and its compounds. This kind of structures are prepared from evaporated and deposited different metals (multi layer technique), which layers have chemical potential gradient, it's a driving force to the diffusion and reaction. Therefore the examination of several bilayers' behaviour is interesting during annealing.

Aims

The basic research works in the topic of diffusion, which can be found in the literature, bring on further questions, on experimental side and on theoretical side also. These questions and answers are collected in this booklet. The applied experimental methods during my work were evolved by the needs of diffusion, which were planned and carried out on the base of literature. From the point of calculation view the basis was the literature, as well. The aim was to develop a model, which can describe the experimental results, which was published earlier in the literature. And to predict other non-measured phenomena (up to now) by means of material parameter's varying. I've searched the answers of the next questions.

Publications

- [1] **Opposits, G.**, Szabó, S., Beke, D.L., Guba, Z., Szabó, I.A., *Diffusion-induced bending of Cu-Ni thin sheet diffusion couples*, Scripta Materialia, **39** (7): 977-983, sep 4 (1998)
- [2] D.L. Beke, **G. Opposits**, I.A. Szabo, *Stress Induced Phenomena on metallization*, Editors: O. Kraft, E. Artz, C.A. Volkert, P.S. Ho, H. Okabayashi, AIP Conference proceedings 491, Melville, New York pp 77-88, (1999)
- [3] I.A. Szabo, **G. Opposits** and D.L. Beke, *Diffusion and Stresses in Multiphase Solids*, Defect and Diffusion Forum, **194-1**: 1431-1436, (2001)
- [4] I.A. Szabó, **G. Opposits** and D.L. Beke, *The effect of stresses on the selection of the Kirkendall marker plane*, Defect and Diffusion Forum, **216-2**: 47-51, (2002)
- [5] I.A. Szabó, **G. Opposits** and D.L. Beke, *Stress in mutual diffusion*, Defect and Diffusion Forum, **216-2**: 13-18, (2002)

Other contributions

- [6] **G. Opposits**, Zs. Gulacsi, *Exact solution for a chain-like cluster growth model for a finite particle size*, Philosophical Magazine B-Physics Of Condensed Matter Statistical Mechanics Electronic Optical and Magnetic Properties, **81** (1): 21-34, jan (2001).
- [7] Schroder DK, Choi BD, Kang SG, Ohashi W, Kitahara K, **Opposits G**, Pavelka T, Benton J, *Silicon epitaxial layer recombination and generation lifetime characterization*, IEEE Transactions On Electron Devices, **50** (4): 906-912, apr (2003)
- [8] **Opposits Gábor**, Valastyán Iván, Trón Lajos, Emri Miklós, *Multimodalitású orvosi képfeldolgozás céljaira kidolgozott absztrakt szoftverkönyvtár*, Hungarian Association for Image Analysis and Pattern Recognition, Conference proceedings IV., Miskolc-Tapolca, 227-231, (2004)

In the first part of my diploma work I examined the interrelation between diffusion and mechanical stresses experimentally. In the second part of my work I examined the diffusion by computer simulation.

Experimental aims

I chose the **Cu-Ni** diffusion pair to my experimental works, and I examined the diffusion-induced deformation in the sample. The examinations were carried out by the technique, which was developed in the Solid State Physics Department of Debrecen University.

- Diffusion induces an anisotropic deformation, so deviations from the ideal cylindrical shape can be experienced. It manifests in the shape of sample: an orthogonal twist is superimposed on the cylindrical deformation. Further on the deformation close to the edge of the sample is sphere shaped (it couldn't be avoided). In the case of ideal cylindrical shape, which was carried out by a technical trick (I embedded **Tungsten** wires in the sample, which works as cross prop). In case of thin sheet diffusion couples, if we measure the curvature with minimal error will the relation between curvature and time be linear?
- In the same system as above, will the atomic currents be influenced by the mechanical stress?
Will the strong porosity formation influence the development of diffusion -that is- will the diffusion zone broadening differ from parabolic law?

Theoretical aims

- Development and analysis of the analytical model, which describes the diffusion and the discussion of different borderline cases.

What kind of closed formula can be given for the verification of calculating in the case of new phase appearing on the basis of the phase growing equations?

Examinations by numerical simulations: what order of magnitude mechanical stress can be localized in the diffusion zone in case of new phase appearing?

- Examination of stable and unstable Kirkendall plane formation in the case of concentration dependent diffusion coefficients. Examinations of stress effects in the case of concentration dependent diffusion coefficients by means of numerical simulations.

I have continued my observations by numerical model [5]. This numerical model can be used for the examination of more phases at the same time [3]. I have carried out the model by means of final difference method.

In case of one phase, the model gave back the others' earlier published results [3].

In the direction of phase growing before the interface mechanical stress accumulated locally in large scale.

In the case of three phases I have examined a new phase, which comes into being in a real experiment *Ni / NiAl₃ / Al*. In this case the stress, developed in the new phase much exceeds the magnitude of GPa, so in case of new phase growing mechanical stresses developed at the interfaces in large scale.

Consequence 4.: The diffusion is either limited by Darken or Nernst-Planck limit (the parabolic law is true for the diffusion length and diffusion time) or the plastic deformation limited (preceding relation is linear). In case of new phase nucleation, the growth rate of new phase can be determined from the diffusion coefficient of each phase and from the concentration at the interfaces. In the direction of phase growing, mechanical stress is accumulated in large scale, which exceeds the magnitude of GPa.

In the following I have supposed a simple exponential dependence for the concentration dependent diffusion coefficient. By choosing a proper concentration dependence of the diffusion coefficient, the location of the maximal velocity moved forward / backward compared to the position of the Kirkendall plane, which corresponded to the unstable / stable Kirkendall plane. [4].

Consequence 3.: The stability of the Kirkendall plane is influenced by the concentration dependence of the diffusion coefficient, very much. I have determined the stress distribution in the case of stable and unstable Kirkendall plane as well.

- I have analyzed the borderline cases of the relaxation process and it's relation by means of the analytical equations of stress effect in thin sheet diffusion couples and in multi layered films [3,5]. There are three well-defined limits: Darken limit (diffusion is limited by the faster component), Nernst-Planck limit (diffusion is limited by the slower component) and the plastic deformation induced limit, where the plastic deformation controls the relaxation process. In the last case strong deviation from the parabolic law of the diffusion zone expansion can be experienced.

I have deduced the equations of the verification method of the numerical calculation by means of the analytical equation of phase growing. Knowing the diffusion coefficients of the two terminal constituents and the new phase, moreover the concentrations at the interfaces (from phase diagram) the phase growth coefficient of the new phase can be calculated.

Results

- The deformation of the samples was an ideally cylindrical, the deformation of the control samples followed the original samples' deformation. So the comparison of the experiment and the theory could be performed. The high precision of measurements was helped by the embedded Tungsten wires ($\varnothing=10\mu\text{m}$), which ensured the ideal cylindrical shape deformation. The scatterings of the bending-time curve points were small [1,2,5].

It turned out, that the bending – time relation is linear, as was predicted by the theory [1,2].

The measured concentration average of intrinsic diffusion coefficient was in good agreement with the data from literature in the whole diffusion zone [1].

The reason of the deviation was the strong void formation in the **Copper** side in all probability. If there were no void formation, the bending and the calculated value would be higher.

The activation energy can be calculated from the bending – time relation. I measured the $\frac{1}{R}(T) = m(T) \cdot t$ relation in my

experiments and the results were good by qualitative. The deviation between the calculated activation energy and the literature can be attributed to the void formation.

It's important to note that the concentration average of intrinsic diffusion coefficient and the activation energy deviates from the literature in a factor 2, in the same direction. Which origins first of all from the void formation induced bending radius increasing.

Consequence 1.: The bending – time relation is linear in *Copper-Nickel* thin sheet diffusion couple. Apart from the void formation, right values can be measured for the diffusion coefficient and the activation energy.

- The relaxation of stress – developed in the diffusion zone – is fast and complete in *Copper – Nickel* system (Darken limit). So the mechanical stress doesn't play role of feedback effect to the atomic currents [1]. It is proven by the fact, that the concentration profile of mechanically constrained samples and non-constrained samples are the same in the order of error limit.

This statement can be proven by experimentally as follows: if the concentration profiles were the same after the Boltzmann transformation (c is represented as the function of $x/\sqrt{t}$), then there is no stress feedback in the atomic currents. Performing this transformation the concentration profiles were the same.

The Boltzmann transformation is sensitive to the diffusion zone expansion's deviation from the parabolic law, which can be modified by the strong void formation (diffusional cross section reduction) in *Copper – Nickel* system. We can deduce from the concentration profiles' similarity, that the void formation doesn't influence this relation [1].

The calculated mutual diffusion coefficient vs. concentration was in good agreement with the literature. It's important to note, that the evaluation wasn't concluded from the sample's bending radius such as in the case of concentration average of intrinsic diffusion coefficient and activation energy. However, in this case the void formation can also modify the results, such as happened in the above-mentioned cases.

The importance of void formation isn't the bending radius changing, but the diffusional cross section reduction. It can be verified by the usage of Boltzmann transformation. It was mentioned earlier, that the concentration profiles were the same after this transformation, so the mutual diffusion coefficient doesn't depend neither on time nor on the magnitude of void formation

Consequence 2.: Stress relaxation is fast and complete in the *Copper – Nickel* thin sheet diffusion couple, so there is no stress feedback to the atomic currents, and the mutual diffusion coefficient is not influenced by the void formation.

- A new result emerged in the topic of Kirkendall plane's nature in the literature nowadays, which augments our knowledge about Kirkendall planes' moving to a new direction. Kirkendall planes may be stable, unstable and there may be more than one in the diffusion zone or there is no Kirkendall plane at all

I have developed the numerical model for case of concentration dependent diffusion coefficient. The stable and unstable Kirkendall planes' moving became traceable with this improved model [4].

I have examined the scale independent solution of the time and distance dependent diffusion equation. By this technique the Kirkendall plane's moving became traceable and it was invariable against scaling.

In the case of constant diffusion coefficient the Kirkendall plane corresponded to the location of the marker position with the highest velocity. [4].