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Andriy M. Gusak

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Andriy M. Gusak

Diffusion-controlled Solid State Reactions

in Alloys, Thin Films, and Nano Systems

With the collaboration of

Yuriy A. Lyashenko

Semen V. Kornienko

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Foreword

I have known Prof. Andriy M. Gusak since 1991, and I visited him in the campus of Cherkassy National University twice. He has visited our campus at UCLA seven times and during each visit he has spent from one to four months in my research group to work together on diffusion-controlled solid-state reactions. It is a topic relevant to processing and reliability of modern microelectronic devices, especially thin film-based devices. For example, metal–silicon reactions are crucial in forming millions of electrical contacts and gates on a piece of Si chip. Another example is Pb-free solder joint reactions in flip-chip technology, which are the most important processing steps in the packaging of consumer electronic products. As we approach the end of Moore's law of miniaturization, a change of paradigm is being developed in order to focus on more applications of the existing CMOS technology besides pushing harder and harder to achieve smaller and smaller devices. When nanotechnology becomes mature and finds applications, diffusion-controlled solid-state reactions in nanoscale materials will be of major concern from the point of view of stability and reliability of the nanodevices.

Prof. Gusak is not only an outstanding physicist, but also a superb mathematician in applying mathematical analysis to new physical findings. He has published many highly cited papers, especially in kinetics of solid-state reactions. He has made significant contributions to reaction kinetics in bulk materials, thin films, and nanoscale microstructures. He has covered kinetic processes from nucleation, growth, to ripening. On reliability issues, he has applied the concept of irreversible processes to electromigration, thermomigration, and stress migration in interconnect and electronic packaging technology. I have benefited tremendously from working with him on the reliability issues, and I appreciate his deep insight and subtle understanding of some of the very salient nature of solid-state reactions.

In this book, Prof. Gusak and his former students have made a systematic presentation of the following topics:

- (i) The initial stages of reactive reactions, including nucleation and lateral growth of nucleated islands. The nucleation of different phases is considered as a coupled process in open systems, under conditions of external fluxes and gradients of chemical potential (Chapters 3, 4, and 5).

- (ii) Other flux-driven processes in open systems leading to specific morphology evolution – flux-drive ripening of intermetallic scallops during reaction between molten solder and metal (copper or nickel), flux-driven lateral grain growth in thin films during deposition, flux-driven bifurcations of Kirkendall planes and the related problem of dynamic stability or instability of these planes, electromigration-driven grain rotation, and electromigration and thermomigration-driven evolution of two-phase alloys (Chapter 6).
- (iii) Void formation, growth, shrinkage, and migration during reactive diffusion in nanoparticles and during electromigration (Chapter 7).
- (iv) Phase growth and competition of growth under stressing by direct electric current (Chapter 8).
- (v) Interdiffusion and reactive diffusion (including the nucleation stage and the formation and growth of two-phase zones) in the ternary systems (Chapters 9 and 10).
- (vi) Special emphasis on diffusion and phase transformations in nanosystems is made in Chapters 2 and 13 (although other chapters, especially Chapter 7, also include some analysis of nanosystems).
- (vii) Since reactions can occur at various ways and proceed in different directions, there are unsolved (in general case) fundamental problems of choice between the evolution paths in closed and in open systems. These topics are intensively discussed in Chapters 11 and 12.

I highly recommend this book to students and to experienced researchers working in the field of materials science, nonequilibrium thermodynamics, and nucleation theory. I am sure it will become a source of new ideas and inspiration for anybody dealing with these topics.

Los Angeles, November 2009

King-Ning Tu

<http://www.seas.ucla.edu/eThinFilm/>

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Editor's Preface

The present book is devoted to solid-state reactions covering the comprehensive analysis of birth (nucleation), growth, and competition of new solid phases as a result of interaction between parent solid phases. So, in order to cope with the theoretical description of such complex processes, the authors have to solve the whole spectrum of problems of description of nucleation and growth that one is confronted with in analyzing such kinds of problems. However, for the systems the authors analyze, additional problems occur, which are of less importance in a variety of other applications. One of them is the existence of a variety of possible reaction channels, the system may evolve at. So, the problem arises, regarding the choice of reaction channels by the systems at given initial conditions. The authors address this problem by connecting the choice of the reaction path with (heuristic) extremum principles for the rate of change of the appropriate thermodynamic functions. Another peculiarity of the analysis of solid-state reactions consists in the existence of well-expressed gradients of the concentration in the solids. These gradients in the concentration may affect significantly the process, and in particular, the work of critical cluster formation and thus the rate of nucleation of new phases.

Having obtained his scientific degrees at Moscow State University, the Institute of Metallurgy of USSR's Academy of Sciences, the Institute for Metal Physics of Ukrainian Academy of Sciences, and Kharkov State University, the leading author of this monograph, Professor Andriy M. Gusak, founded and now heads a highly productive group of applied theoreticians (at Cherkassy National University) involved in theoretical and computer modeling of diffusion, reactions, electromigration, void migration and microstructure change in metals, metal junctions, and nanosystems. Awarded with many prizes (among them a prize awarded by the American Physical Society) for his work, he has worked jointly as an investigator with several international teams and served on international advisory boards for major conferences in the field of nanoscience. Scientific visits have taken him to prestigious universities of Göttingen, Münster (Germany), UCLA (USA), Singapore, Grenoble, Marseille (France), Eindhoven (Netherlands), and Krakov (Poland). Written by an author with comprehensive and international expertise in cooperation with his young coworkers, the monograph coherently and comprehensively presents the approaches and results hitherto only available in various journal papers and at part only in Russian or Ukrainian language.

The editor of the present monograph had the pleasure to discuss a variety of problems outlined in the present book on several research workshops in Dubna (Russia) devoted to the general topic “Nucleation Theory and Applications.” In his research, Professor Gusak and his colleagues always combined profound theoretical analysis and applied research. In this way, the present book is not only of interest for people dealing with the theoretical concepts of phase formation but a must-have for all those involved with the public or corporate science of nanosystems, thin films and electrical engineering, and their applications.

Rostock and Dubna, December 2009

Dr. habil. Jörn W. P. Schmelzer

List of Contributors



This book is written by a group of applied theoreticians headed by **Prof. A. M. Gusak** and working at Cherkassy National University, Ukraine. The group is well-known, first of all, in the international diffusion community for their successful combination of deep insight into diffusion-controlled processes employing relatively simple mathematical tools for modeling these processes. The Cherkassy group has established long-standing cooperation links with diffusion and reactions centers in Debrecen, Eindhoven, Ekaterinburg, Göttingen, Grenoble, Kiev, Kharkov, Krakow, Los Angeles, Marseille, Moscow, Muenster, Rostock, and Singapore. The group is known also for organizing periodic international DIFTRANS conferences. The group and its members have obtained various international grants (International Science Foundation, CRDF, INTAS, etc.) The group includes:



Yuriy A. Lyashenko PhD (1992). Dean of Physics School. Having graduated from Cherkassy National University with the degree in physics, he defended his PhD thesis at G. V. Kurdyumov Institute for Metal Physics of the Ukrainian Academy of Sciences in Kiev. His field of expertise includes interdiffusion in ternary single-phase and two-phase alloys, cellular precipitation, diffusion induced grain-boundary migration, application of extremum principles to the description of complex systems.



Semen V. Kornienko PhD (1999). Chair of Theoretical Physics. Having graduated from Cherkassy National University with the degree in physics, he defended his PhD thesis at Kharkov National University. His field of expertise includes nucleation, inter- and reactive diffusion in ternary systems, phase growth under electromigration, diffusion with nonequilibrium vacancies.



Aram S. Shirinyan PhD (2001). Associate Professor in theoretical physics, now working on his habilitation thesis at T. Shevchenko National University in Kiev. He obtained his scientific degrees at Erevan State University, Armenia (1993), Cherkassy National University (1998), and Kharkov National University (2001) in solid-state physics. He has been awarded with the personal scientific grant of the Ukrainian Government, honorary diploma of the National Academy of Sciences of Ukraine (2002). He has profound experience in international cooperation (INTAS individual grant (2004), DAAD fellowship (2008), primary investigator in a joint Ukrainian–German project (2009) etc.), the main scientific contacts are established to colleagues in Bulgaria, Belgium, France, Germany, Hungary, Poland, Russia, USA. His field of expertise is in materials science, condensed matter physics, nanophysics, reaction–diffusion processes, and phase equilibria in low-dimensional and, in particular, nanosize systems, thermodynamics and kinetics of first-order phase transitions in multicomponent systems.



Mykola O. Pasichnyy PhD (2006). Chair of General Physics. Having graduated from Cherkassy National University with the degree in physics, he defended his PhD thesis in solid-state physics at the G. V. Kurdyumov Institute for Metal Physics of the Ukrainian Academy of Sciences in Kiev. The thesis was directed to the modeling of the initial stages of solid-state reactions. His field of expertise is in the theory and modeling of new phase nucleation, growth and competition during reactive diffusion or decomposition.



Tatyana V. Zaporozhets PhD (1999). Associate Professor at the Department of Theoretical Physics. Currently working on her habilitation thesis. Having graduated from Cherkassy National University with the degree in mathematics, she defended her PhD thesis in solid-state physics at the G. V. Kurdyumov Institute for Metal Physics of the Ukrainian Academy of Sciences in Kiev. Her field of expertise includes computer modeling of phase transformations and reactive diffusion in solids with preference to simulation at an atomic level by Monte Carlo methods, molecular dynamics, and molecular statics. She likes to confirm, visualize, and adorn the elegant but somewhat dull and long formulae derived by Prof. Gusak.