

BOOK REVIEW

Interfaces in crystalline materials (1996) A. P. Sutton, R. W. Balluffi

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The interfaces with which this impressive volume deals are not the ones that usually concern electrochemists. It is therefore all the more attractive to enter this world, a world which will certainly grow much more in significance for electrochemical studies, especially those of solid state electrochemistry, where interfaces in crystalline materials are ubiquitous.

The book is divided into four parts, 'Interfacial Structure', 'Interfacial Thermodynamics', 'Interfacial Kinetics' and 'Interfacial Properties'. No other book attempts to give a comparable comprehensive and conscious description of this wide scientific field. The treatment is suitable for both postgraduate students and scientists who need information on interfaces. The authors give a very helpful glossary of terms related to interfaces at the very beginning of the text.

Part I, 'Interfacial Structure', starts with a chapter on 'The geometry of interfaces', including some basic group theory, geometric relationships between two crystals and the geometrical specification of interfaces, followed by a description of bicrystals and examples of the interfaces of lattice-matched polar-non-polar epitaxial interfaces and lattice-matched metal-silicide silicon interfaces. Later, a classification of isolated interfacial line defects is given. The second chapter of Part I is devoted to 'Dislocation models for interfaces'. This is very well illustrated, making it easy to understand the theoretical formation of grain boundaries and heterophase interfaces which are free of long-range stresses. The third chapter of Part I deals with 'Models of interatomic forces at interfaces'. There are as important as the geometric constellations of interfaces. In this chapter, the authors introduce the reader to the most important theories of how to describe interatomic forces in condensed matter. A major point of this part is the discussion of the relationship between these forces and the local atomic environment. The last chapter of Part I is entitled 'Models and experimental observations of atomic structure'. After a classification into sharp and diffuse homophase and heterophase interfaces, there follow examples of computer-simulated interfaces as well as high-resolution electron microscopic pictures. As to the case of heterophase interfaces, the metal-insulator interfaces are discussed with respect to wettability studies (contact angle method). The chapter closes with metal-semiconductor interfaces, paying special attention to the epitaxial layers of NiSi₂ and CoSi₂ on silicon.

Part II of the volume, entitled 'Thermodynamics of Interfaces', starts with the interface free energy and its relation to other interface thermodynamic quantities. Later, the authors discuss the 'interface stress' as an excess thermodynamic quantity which is generally associated with any interface. They derive the relationship between the surface stress and the surface free energy and finally give the example of a small sphere of a phase α embedded in a phase β under the condition that the volume of a sphere α is larger than the volume which is available for it in phase β . This is an interesting and important case for which the final stress (hydrostatic pressure) in the spherical particle is calculated. Next, the effect of interface geometry on thermodynamic variables is discussed. The Wulff plot showing the dependence of interface free

energy on inclination is introduced, and the equilibrium shape of embedded second phase particles is considered. Further, the shaping of interfaces as a result of minimizing the interface free energy is shown. This effect leads to the formation of 'hill and valley' structures in some cases. This is followed by a description of the theory of capillary pressure associated with curved interfaces and the treatment of the equilibrium lattice solubility at curved heterophase interfaces and at embedded second-phase particles. The dependence of the interface energy on crystal misorientation and variations of crystal misorientation follow. In the next section, chemical potentials and so-called diffusion potentials are discussed as the thermodynamic driving forces for diffusion processes at interface systems. The chapter on thermodynamics closes with a thorough discussion of 'interphase phases' and their phase transitions, while the last chapter of Part II is devoted to segregation processes, i.e. the enrichment of atoms of one phase at the interface. This phenomenon is illustrated by a number of experimental findings, and various physical models for the theoretical description of this kind of adsorption at interfaces are given.

Part III, entitled 'Interfacial Kinetics', starts with a thorough description of the diffusion at interfaces and the different diffusion regimes encountered in polycrystals (Chapter 8). The fast diffusion along interfaces of species which are substitutional in the crystal lattice is very impressively illustrated by a number of Arrhenius plots from very recent studies of metal systems. This is followed by examples of diffusion studies of ionic systems, including those of interest to electrochemists, e.g. Cu₂O, NiO, ZrO₂, etc. Considerable space is devoted to the effects of the interface structure on diffusion and to the mechanisms of diffusion at grain boundaries. This chapter also includes the treatment of diffusion along interfaces of solute species which are interstitial in the crystal lattice and the interesting case of *slow* diffusion across interfaces in *fast* ion conductors, e.g. β -alumina. Finally, the phenomenon of diffusion-induced grain boundary motion is briefly described. At this point, the reader is prepared to understand the conservative motion of interfaces (Chapter 9), which means the motion of interfaces with no net diffusion flux of any component. These are extremely important processes, which comprise recrystallisation within polycrystalline solids and also phase transformations. The driving pressure for such conservative motions can range from 10³ to 10⁹ Pa. Chapter 10 deals with the non-conservative motion of interfaces. A non-conservative interface motion needs the interface to act as a source or sink of atoms with respect to the adjoining lattice.

The last part of the book, entitled 'Interfacial Properties', makes use of the fundamentals discussed in the foregoing parts and is focussed on (a) electronic and (b) mechanical properties of interfaces. These properties are certainly most important for modern technology. The electronic properties of all semiconductor devices depend, deliberately or not, on the electronic situation at hetero or homo phase boundaries. Consequently, the authors have included information on metal-semiconductor interfaces, semiconductor heterojunctions, grain boundaries in metals and semiconductors, and high-temperature superconductors. Among the mechanical properties, the following are discussed: compatibility stress caused by applied elastic stress, plastic straining, and heating or cooling. The authors explain how interfaces may act themselves as sinks of lattice dislocation and also as sources of both interfacial

and lattice dislocations. A Chapter on the fracture at homophase interfaces concludes this part.

With this volume, A. P. Sutton and R. W. Balluffi have succeeded in presenting a very complex matter in a readable and understandable way. Mathematics has been kept to a minimum and is easy to follow. Though there are certainly aspects which the occasional reader will miss, the book is overall of superior quality and can be expected to become a classical reference source for

many years to come. For a future edition, one would hope for a substantial extension of the index, as there are hardly any references to the many examples given throughout the text. This volume can be warmly recommended to everybody who is engaged in solid state electrochemistry.

Fritz Scholz, Berlin