Defect and Diffusion Forum Vols. 194-199 (2001) pp 1001-1008
online at http://www.scientific.net

Chemical Diffusion Across Grain Boundaries: In-Situ Observation and Phenomenological Modeling

J. Jamnik, M. Leonhardt and J. Maier

Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, DE-70569 Stuttgart, Germany

Keywords: Chemical Diffusion, Grain Boundaries, Optical Spectroscopy, Schottky Barrier, $SrTiO_3$

Abstract. In this paper we report two recent achievements with respect to chemical diffusion across grain boundaries:

(i) A model based on the concepts of electrostatic and chemical capacitances and electrochemical resistances is introduced. This model, which is derived from the Nernst-Planck-Poisson equations, turns out to be a very efficient tool yielding an adequate description of chemical diffusion across Schottky barriers.

(ii) The model predictions were verified by a novel method which allows for insitu monitoring of the diffusion front as it propagates across a single grain boundary in Fe- doped $SrTiO_3$. The low symmetry boundary (near $\Sigma 13$) shows a pronounced chemical resistance reflected by a distinct jump in the concentration profiles, while the highly symmetrical $\Sigma 3$ boundary is not of any measurable influence. The effects can be quantitatively explained by Schottky barriers acting on both electrons and ions. The diffusion profiles can be precisely modelled with the space charge potential as the only unknown parameter. The space charge potentials are found to be in good agreement with the values derived from electrical measurements.

Introduction

Chemical diffusion describes the transport of a neutral component in a nonstoichiometric compound under a chemical potential gradient. Since the mobile species in prevalently ionic crystals are charged, chemical diffusion is composed of ambipolar fluxes of at least two species. In the simplest case these are ions and electrons, e.g. O^{2-} and $2e^-$ for oxygen transport in an oxide.

Chemical diffusion is an important process for the preparation, functioning and degradation of many materials. It controls the kinetics of compositional changes (sensors, intercalation electrodes in batteries), leads to selective permeation of gases (gas separation membranes), allows for extension of electrochemical reactions from triple to two phase boundaries (electrode kinetics in solid oxide fuel cells), etc.

In polycrystalline materials and composites the transport of mobile species, and thus also chemical diffusion, is influenced by internal boundaries. Unlike in metals, in oxide ceramics, for example, the interfaces can act as hindrances for the transport as well as fast pathways. Moreover, the diffusion coefficient for transport along an interface may distinctly differ from the diffusion coefficient for transport across that interface. While chemical diffusion in electroneutral grains is reasonably well understood, transport along [1-3] and/or across [4] the boundaries and sample surfaces has much less been treated. There is a lack of experimental techniques, as well as of theoretical models. Spatial heterogeneity enormously complicates the problem since the transport coefficients for ions and electrons may exhibit different spatial dependence. There could be different pathways for the two carriers, but on the other hand, the carriers are charged and thus coupled electrostatically.

Report Documentation Page	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE **JUL 2000**	2. REPORT TYPE	3. DATES COVERED **00-00-2000 to 00-00-2000**

4. TITLE AND SUBTITLE **Chemical Diffusion Across Grain Boundaries: In-Situ Observation and Phenomenological Modeling**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Max-Planck Institut fur Festkorperforschung,Heisenbergstrasse 1,DE-70569 Stuttgart, Germany,**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S)
	11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

See also ADA392907. Proceedings of DIMAT2000, The Fifth International Conference on Diffusion in Materials, Paris, France, July 17-21, 2000. U.S. Government or Federal Rights License.

14. ABSTRACT

see report

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**7**	

In this paper we focus on a very simple microstructure as provided by a bicrystal. As a model material we use Fe–doped $SrTiO_3$. The bulk defect and transport properties of this perovskite are well-known [5]. Even more, the electronic resistances of the grain boundaries have been studied in depth and described by cusp-like double-Schottky barriers [6-8]. Chemical diffusion, however, is more complex than electronic conductivity. We first present the model for chemical diffusion across Schottky barriers and then describe the novel experimental technique which we used to detect in situ the impact of $\Sigma 3$ and $\approx\Sigma 13$ grain boundaries on oxygen diffusion.

Phenomenological model

We consider an inward diffusion of oxygen into the bicrystal as shown in Fig. 1. Phenomenologically, the description is simple. Diffusion in the bulk parts of the bicrystals follows Fick's law.

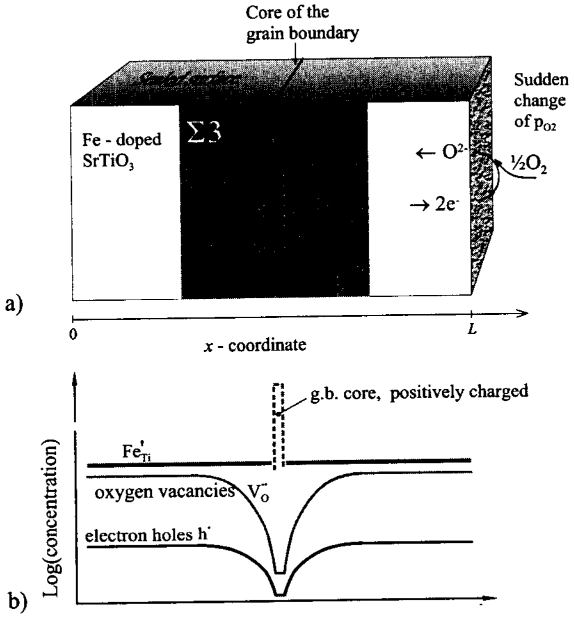

Fig. 1: a) Scheme of the bicrystal. b) Cusp-like double-barrier model of the grain boundary.

Assuming that the oxygen partial pressure outside of the crystal changes in a stepwise manner, the oxygen incorporation at the surface can be taken into account by the boundary condition [9],

$$J_O = -k_s(c_\infty - c(t)), \tag{1}$$

k_s being the rate constant of the overall reaction, c_∞ the edge concentration reached at the end of the experiment and J_O the oxygen flux density. The transport through the boundary can be described by a similar ansatz,

$$J_O = -k_{gb}(c''-c'). \tag{2}$$

Symbols, c'' and c', denote the concentrations at the right hand side and left hand side of the boundary, respectively. On this level the interfacial rate constant, k_{gb}, is just a phenomenological parameter. If we want to learn more about k_{gb}, for example its dependence on the boundary structure, or its dependence on space charge layers, or if we are simply interested in the validity range of the ansatz, a more detailed model is necessarily.

Drift-diffusion model

On the continuum level chemical diffusion can be described by the drift-diffusion model. We neglect morphological changes and assume that the externally applied chemical potential gradient is small. Then the flux densities of ionic and electronic carriers follow from the linear equations of irreversible thermodynamics, to which we add the continuity equations and, since the carriers are charged, the Poisson equation (Nernst-Planck-Poisson equations). The materials parameters which appear in this model are initial concentrations of the carriers, their mobilities, charge numbers, and the dielectric constant of the material [4,10].

Within the grain boundary region these parameters may deviate from the bulk values (this is the definition of the grain boundary on the continuum level). Fig. 1 shows the atomistic structure of the $\Sigma3$ boundary obtained by transmission electron spectroscopy [11]. In the first approximation we may assume that the structure is, except in the core, spatially invariant. Thus, for the carrier mobilities we may use the bulk values (neglect in this instance the effects of the core on the mobilities). Regarding the carrier concentrations the space charge model of the boundary will be used. So far the model proved to be very reliable in considerations of the electronic properties of this material [6-8]. According to the model there is a positive charge trapped in the core of the boundary. The counter charge density is essentially given by the dopant (Fe^{3+}) within the space charge layers, while the positively charged oxygen vacancies and holes are depleted in that regions. Thus the only interfacial parameter is the height of the Schottky barrier, i.e. the electric potential difference between the core and the bulk, $\Delta\phi$.

We can now simulate the time and position dependent carrier concentrations as they evolve, e.g. upon a sudden change of the oxygen partial pressure at the right hand side of the bicrystal, while keeping the partial pressure at the left side of the crystal constant. Fig. 2 shows the deviation of the oxygen vacancy concentration from its initial values. We assumed here, for simplicity, that the surface reactions are very fast, and that the mobilities of ionic and electronic carriers are equal. As we see in Fig. 2, the Schottky barrier perceptibly hinders the chemical diffusion. The concentration profiles within the space charge layers are quite complicated: at both edges the flux flows in the direction of increasing concentration, which obviously reflects the presence of kinetically induced position dependent electric fields.

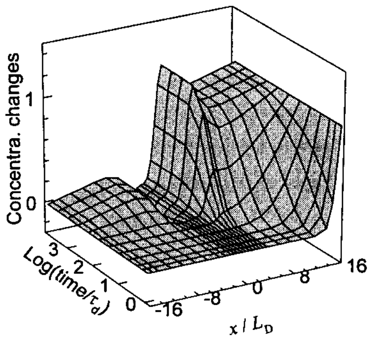

Fig. 2: Simulated changes of the oxygen vacancy concentration from initial values upon sudden change of the oxygen partial pressure at the right hand side of the bicrystal. The thickness of the bicrystal is 32 Debye lengths, the boundary is located at x=0. The time scale is normalised with respect to the dielectric relaxation time. For details see Ref. [10].

The numerical solution of the drift-diffusion model can be used to fit the measured data. It is, however, still of interest to determine the relation between the numerical results and the parameters of the phenomenological model, e.g. the dependence of k_{gb} on the barrier height. After all, it should be possible to show that the phenomenological model is just a limiting case of the drift diffusion one. To demonstrate this we use another tool [12], i.e. the equivalent circuits for diffusion. Fig. 3a shows the equivalent circuit, which corresponds exactly to the drift diffusion model. Besides the familiar elements, ionic and electronic resistances, electrostatic capacitors, also chemical capacitors appear in the circuit. They are defined as, $C_j^\delta = (ez_j)^2(\partial\mu_j/\partial c_j)^{-1}V$, V being the volume, μ_j the chemical potential, z_j the charge number and e the absolute value of the electronic charge. Chemical capacitors describe the ability of the material to accept or release charge carriers upon small changes of the carrier's chemical potential. The external oxygen chemical potential is taken into account by a "chemical potential source" and the incorporation kinetics by the resistance R_s.

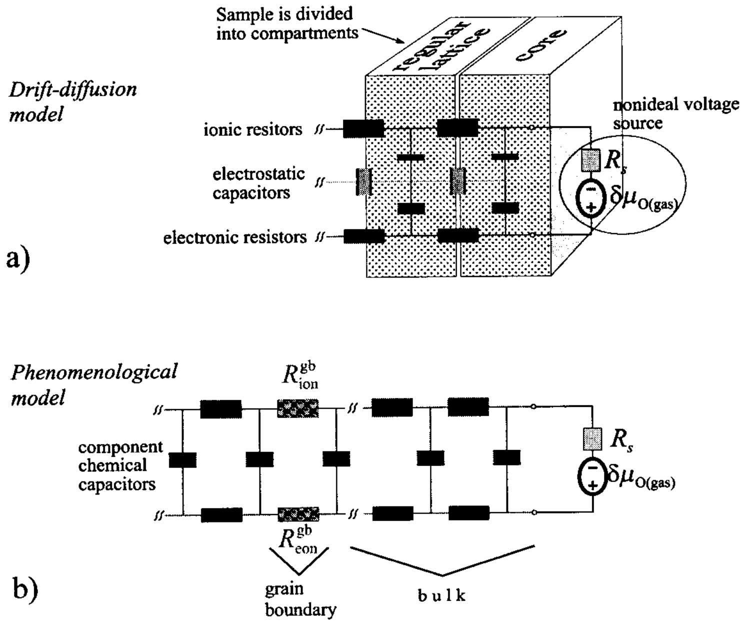

Fig. 3: a) Exact equivalent circuit according to drift-diffusion model.
b) Reduced circuit.

If we focus on time scales large compared to the dielectric relaxation time, and if the spatial resolution of interest is above the Debye length, the electrostatic capacitors can be omitted. If the volume fraction of the grain boundary regions is small, we may also neglect the chemical capacity associated with the grain boundaries, as the chemical capacity is proportional to the volume. Such a reduced circuit, as shown in Fig. 3b, corresponds exactly to the phenomenological model. Denoting the bulk ionic and electronic resistances by R_{ion} and R_{eon}, the entire bulk chemical capacitance of oxygen by, C^δ, and the sample length by L, the diffusion coefficient reads $D^\delta = L^2/((R_{ion}+R_{eon})C^\delta)$, the surface rate constant $k_s = L/(R_s C^\delta)$, and more importantly, $k_{gb} = L/((R_{ion}^{gb}+R_{eon}^{gb})C^\delta)$. In the last expression only the resistances refer to the grain boundary: $R_j^{gb}(\Delta\phi) = \int_{gb}\sigma_j^{-1}(x;\Delta\phi)dx$, where σ_j denotes the conductivity profile. If $R_{ion} >> R_{eon}$, k_{gb} depends essentially on the ionic resistance, thus $k_{gb} \propto \exp(-2\Delta\phi/k_B T)$, while the electronic resistance, which is measured electrically, is proportional to $\exp(\Delta\phi/k_B T)$ (k_B and T denote the Boltzmann constant and the temperature respectively). This conclusion was verified with the experiment described in the next section.

Experimental

Fe-doped $SrTO_3$ has the interesting property that its optical absorption (colour) depends on the stoichiometry. Thus, using spatially resolved optical spectroscopy, we could monitor in-situ how the diffusion profile evolves within the crystal [13]. Figs. 4a) and b) show "snap shots" taken during the diffusion through $\Sigma3$ and $\approx\Sigma13$ grain boundary [14]. The extracted concentration profiles are displayed in Figs. 4cd. The scattered data refer to measurements while the solid curves reflect the fit using the phenomenological model. Besides the rate constant for the surface incorporation, k_s, the only adjustable parameter was the height of the Schottky barrier. We see that the fit is quite good, which justifies the assumptions made (neglected chemical capacity of the grain boundary, etc.).

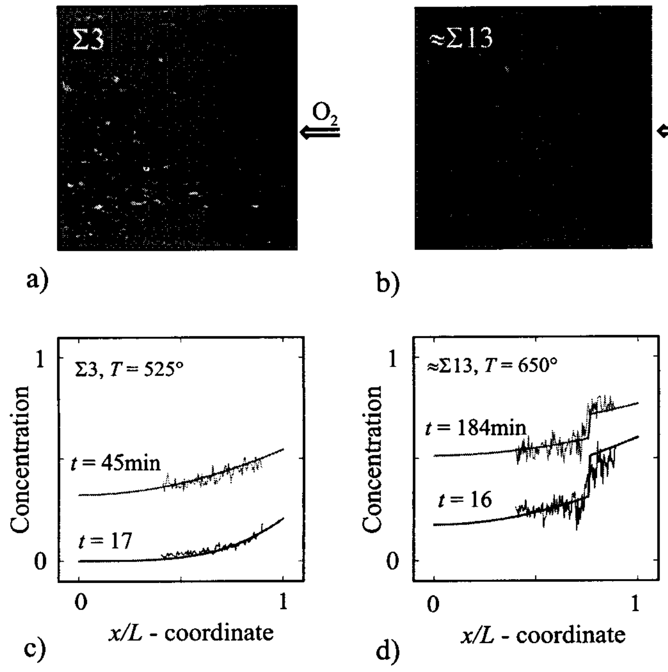

Fig. 4: a,b) Snapshots of inward diffusion of oxygen through two different grain boundaries. b,c) The concentration profiles derived from the set of such data as shown in Fig. 4ab. Solid lines refer to the fit.

In the case of $\Sigma3$ boundary, the impact of the grain boundary was below the detection limit. The more disordered $\approx\Sigma13$ boundary, on the other hand, clearly hinders the propagation of oxygen. In Fig. 5 the obtained $\Delta\phi$ is compared with the height of the barrier as deduced from the measured electronic resistance of the boundary. The extraction of $\Delta\phi$ relies on assuming the Fe-concentration profile within the space charge regions. Since the actual profile is not known two limiting cases were considered in the analysis: (i) flat Fe-profile (Schottky-Mott model) and (ii) equilibrium Fe-profile (Gouy-Chapman model). As shown in Fig. 5, the choice of the model is not important in the high temperature range (chemical experiment), while at lower temperatures (electrical experiment) Fe-profile is most likely flat due to poor mobility of Fe. Taking this into account, the agreement between the chemical and electrical experiments is good. Recently the model has been confirmed by the electrical measurements of electronic and ionic boundary resistances separately [16]. Nearly T-independent $\Delta\phi$ is not unexpected: if the interfacial (core) levels are deep, the charge trapped there is "frozen-in". Finally the question remains why $\Delta\phi_{\Sigma13} > \Delta\phi_{\Sigma3}$. Although a precise answer requires an atomistic model of the interface, intuitively this is not surprising; the $\approx\Sigma13$ boundary provides a much stronger break of symmetry than the $\Sigma3$ boundary.

Conclusions

We detected insitu the evolution of concentration profiles associated with the oxygen diffusion through grain boundaries. Applying the drift diffusion model for chemical diffusion and assuming the space charge model for the grain boundaries with respect to both electronic and ionic carriers we calculated from the measured profiles the space charge potentials. The values obtained, ≈0.5V, are in good agreement with independently measured electronic resistances of the grain boundary. The Σ3 boundary which represents a much smaller structural perturbation exhibits a significantly smaller space charge potential of ≤ 0.3V.

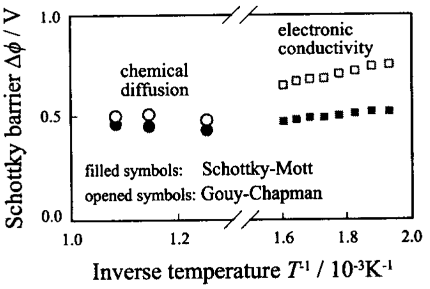

Fig. 5: Temperature dependence of the height of the Schottky barrier in ≈Σ13 grain boundary derived from chemical and electrical experiment.

References

[1] M. Backhaus-Ricoult and A. Peyrot-Chabrol, Philosophical Magazine A Vol. 73 (1996), pp. 973 ff.

[2] H.D. Wiemhofer, T. Hauber and B. Stroetmann, Defect Diffusion Forum Vol. 143, (1997), pp. 1323 ff.

[3] J.R. Lagraff and D.A. Payne, Phys. Rev. B Vol. 47 (1993), pp. 3380 ff.

[4] I. Lubomirsky, K. Gartsman and D. Cahen, J. Appl. Phys. Vol. 83 (1998), pp. 4678 ff.

[5] I. Denk, W. Munch and J. Maier, J. Am. Ceram. Soc. Vol. 78 (1995), pp. 3265 ff.

[6] R. Waser and R. Hagenbeck, Acta Materialia Vol. 48 (2000), pp. 797 ff.

[7] J.H. Hwang, K.D. Johnson, T.O. Mason and V.P. Dravid, Applied Physics Letters Vol. 76 (2000), pp. 2621 ff.

[8] T. Kawada, N. Iizawa, M. Tomida, A. Kaimai, K. Kawamura, Y. Nigara and J. Mizusaki, J. European. Ceram. Soc. Vol 19 (1999), pp. 687 ff.

[9] J. Crank, *The Mathematics of Diffusion*, (Clarendon Press, Oxford, 1990, pp 9).

[10] J. Jamnik and J. Maier, J. Electrochem. Soc. Vol. 145 (1998), pp 1762ff.

[11] O. Kienzle, F. Ernst, J. Am. Ceram. Soc. Vol. 80 (1997), pp 1639ff; O. Kienzle, Ph.D.-Thesis, University of Stuttgart, 1999.

[12] J. Jamnik and J. Maier, Physical chemistry chemical physics, submitted.

[13] T. Bieger, J. Maier and R. Waser, Ber. Bunsen.-Ges. Phys. Chem. Vol 97 (1993), pp 1098ff.

[14] M. Leonhardt, J. Jamnik and J. Maier, Electrochemical and Solid State letters Vol. 2 (1999), pp 333ff.

[15] M. Leonhardt, Ph.D.-Thesis, University of Stuttgart, 1999.

[16] X. Guo and J. Maier, in preparation.

Mishin: Will the blocking effect show up if you measure the chemical diffusion coefficient on a polycrystal? It seems that in this case, the diffusion will be dominated by fast diffusion along parallel grain boundaries?
A: If the grain boundary diffusivity is indeed faster than the bulk diffusivity (in oxides this is not automatically the case) and if the highly conductive grain boundaries form continuous paths, then the blocking effects are not expected to show up. Percolation depends of course on the particular microstructure. We do not have many experimental data on chemical diffusion in polycrystals. Measurements of electrical conductivity and tracer diffusion support this.

Rabkin: Have you observed any GB migration during oxygen diffusion?
A: We did not. We did experiments at temperature below 700°C, the oxygen partial pressure changes were about one order of magnitude. Under this conditions the concentrations and probably also the mobilities of Sr and Ti defects are very low compared to oxygen vacancies.