



## ZnO Grain Boundaries: Electrical Activity and Diffusion

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**Abstract.** The operation and performance of electroceramics are commonly dependent on the characteristics of electrically active grain boundaries. To date, our understanding of the role of specified additives and heat treatments on the grain boundary properties remains underdeveloped. We describe efforts directed towards improving our understanding by (a) fabrication and analysis of individual boundaries, (b) improved control and simplification of boundary chemistry (c) systematic investigation of properties (e.g.,  $I$ - $V$ , DLTS,  $D_O$  and  $D_M$ ) as a function of boundary structure and chemistry and (d) development of appropriate energy band, defect and diffusion models. Following this approach, preliminary results suggest that lattice defects play critical roles in controlling both the electrical and diffusive properties of the boundaries while the additives appear to act in supportive manner by activating the key lattice defects particularly with respect to the electrical activity of the boundaries.

**Keywords:** varistor, ZnO, grain boundary, DLTS, diffusion, interface states

### Introduction

Traditional electronic devices depend for their operation on the existence of many individual, highly controlled and reproducible electrically active junctions. This reflects, according to one estimate, the production of approximately  $10^{17}$  silicon p-n junctions per year. Electroceramics, being largely polycrystalline, also possess large numbers of interfaces which, when appropriately doped or modified, control the electronic properties of these devices. However, unlike integrated circuits, for which one uses parallel planar processing to fabricate many thousands of near identical junctions, electroceramics are characterized by inhomogeneities generated during the powder preparation, compacting and sintering processes. This results in non-uniform grain size, porosity, impurity segregation, grain-grain misorientation and second phase distribution. The large number of grain boundaries with varying characteristics, connected both in series and in parallel, form rather complex three-dimensional networks. As a consequence, it becomes difficult to

understand the characteristics of individual boundaries by measuring the overall electrical properties of an electroceramic device. Likewise, it complicates the prediction of device characteristics by reference to a simple grain boundary model.

ZnO, the subject of this article, has been used for years as an overvoltage protection device. Such varistors (voltage variable resistors) exhibit highly nonlinear current-voltage ( $I$ - $V$ ) characteristics illustrated in Fig. 1. The high resistance at low voltage is attributed to the existence of double schottky barriers at the grain boundaries. A schematic of such a barrier is illustrated in Fig. 2. Here, interface states trap electrons from the adjacent grains, inducing the formation of electron depleted regions adjacent to the boundaries and corresponding space charge barriers. Typical values for the barrier height ( $\Phi_B$ ), space charge width ( $x_0$ ), interface density ( $N_i$ ) and dopant density ( $N_0$ ) are 1 eV, 500–1000 Å,  $10^{12}$  cm<sup>-2</sup> and  $10^{18}$  cm<sup>-3</sup> respectively [1].

The general features necessary to induce such nonlinearities at grain boundaries in ZnO have been known for some time. The key ingredients include the

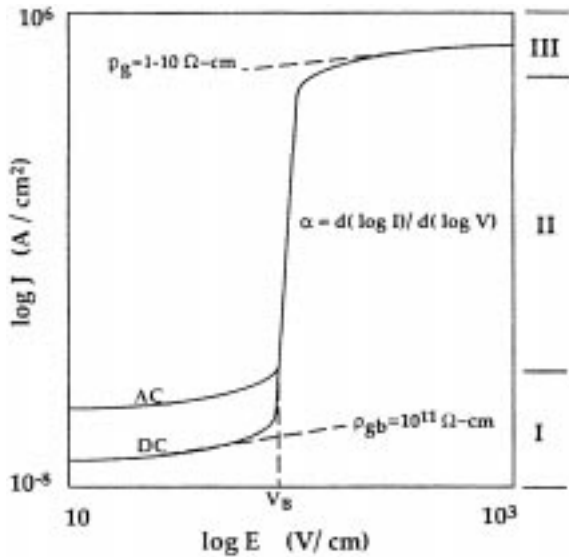


Fig. 1. *I-V* curves for a ZnO varistor showing three distinct areas of operation: prebreakdown, breakdown and ohmic behavior.

addition of (1) deep donors (e.g., Co, Mn) and (2) segregants (e.g., Bi, Pr) and the performance of an (3) oxidative anneal [2]. Nevertheless, the precise role of each of these ingredients in influencing the operating characteristics of varistors has yet to be determined.

To further our understanding of grain boundary phenomena, advances in control and characterization of grain boundary chemistry and structure are required. Since one boundary may differ from the next, electrical characterization of individual boundaries must be pursued. Grain boundary diffusion often controls boundary chemistry and so must be examined in a more complete fashion than in the past. Finally, as in the bulk, an understanding of the defect chemistry at the boundaries is essential for understanding barrier formation, mass transport and aging of barriers. Recent progress achieved along these lines at MIT is summarized in this article.

**Single Barrier Studies**

Individual boundaries can be prepared and/or examined in a number of ways. One of the most obvious is to attach electrodes to adjacent grains in a polycrystalline specimen by use of microprobe needles [3] or suitable photoresist metallization patterns [4,5]. These arrangements are illustrated in Fig. 3. *I-V* character-

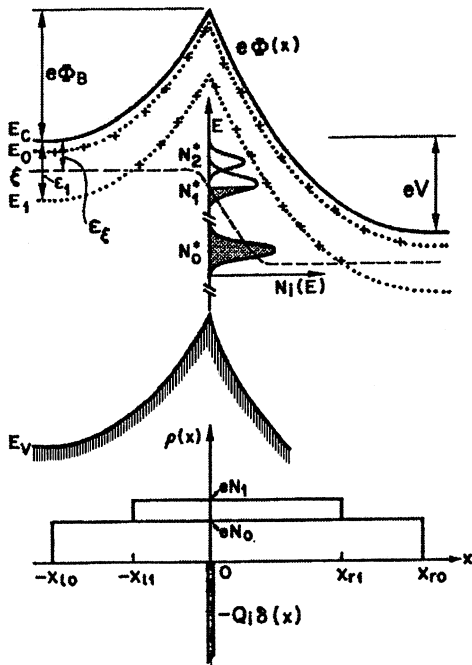


Fig. 2. Double Schottky barrier at a negatively charged grain boundary showing spatial dependence of band bending  $e\Phi(x)$ , density of states distribution of interface traps  $N_i(E)$  and charge density distribution  $\rho(x)$ . From Greuter et al. [1].

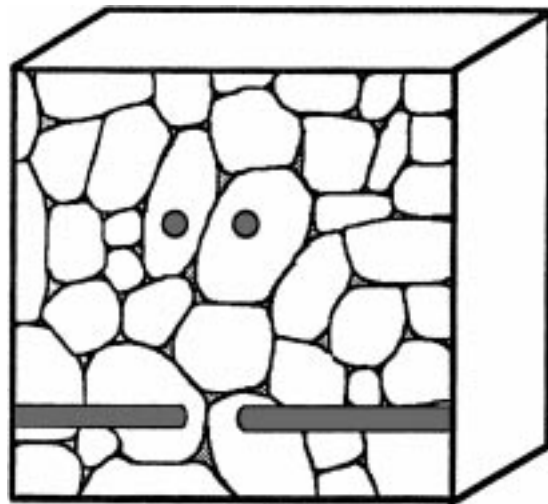


Fig. 3. Schematic of polycrystalline ceramic with microprobe needle electrodes or lithographically defined metallizations placed to measure the electrical properties of individual grain boundaries.

istics of individual boundaries can then be correlated with the local structure by electron microscopy [6]. Although microcontacts can be directly applied to specific boundaries, alternate conduction paths, bypassing the boundary of interest, are not entirely eliminated unless further efforts are made to thin the specimens and isolate the specific grain-grain pairs of interest [7].

Alternatively, one may fabricate artificial single barrier structures by applying activating dopants between single crystals to form bicrystal-like structures [8]. Since the additives can be tailored, then the interfacial chemistry is, in principle, controllable and can be related to the electrical properties. However, microscopic inspection of these structures reveals a thick, intervening additive layer between the 'simulated' grains. This is not representative of real varistor microstructures and is more accurately described as an oxide heterojunction rather than a homojunction.

Our laboratory has reported the successful forma-

tion of single, electrically active ZnO grain boundary interfaces by the surface in-diffusion (SID) method [9,10]. In this process, the chemical additives are sandwiched between two polycrystalline specimens (often un-doped) and then heated for a controlled time and temperature to achieve an effective in-diffusion distance of one or more grain distances. The  $I$ - $V$  characteristics of such a structure (see Fig. 4) show that an "effective" single interface has been activated with a breakdown voltage of about 3 V and nonlinearity factor  $\alpha \sim 12$ . Due to possible uneven in-diffusion through the network of grain boundaries, the leakage current in these specimens is typically higher than those obtained in conventional devices. We are presently extending this approach to the growth of thin textured films by vapor transport or sputtering techniques. In this manner, one obtains grains aligned with their  $c$ -axes perpendicular to the substrate plane. This provides for more uniform diffusion pathways.

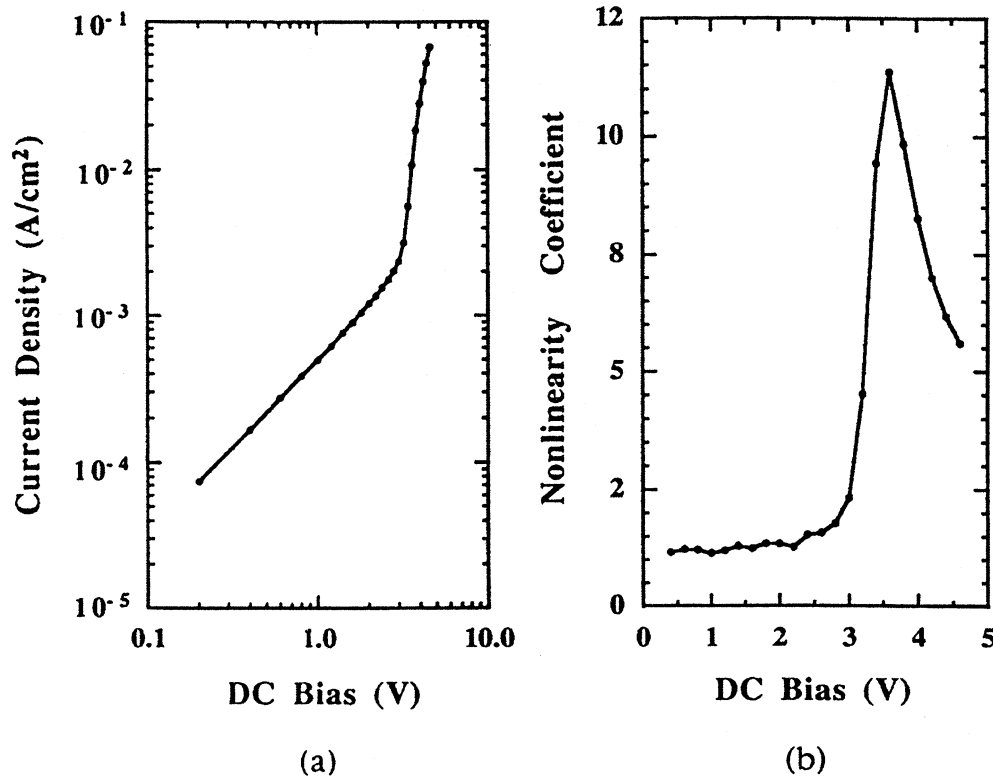


Fig. 4.  $I$ - $V$  and nonlinear coefficient  $\alpha$  versus voltage bias for a Pr/Co-doped SID ZnO varistor showing  $\sim 3$  V breakdown voltage and peak  $\alpha$  approaching a value of 12. From Tuller and Baek [10].

### Boundary Chemistry

ZnO varistors require certain additives and heat treatments resulting in the enrichment of species such as Bi and O at the grain boundaries. Greuter et al. [1] found, for example, that a decrease in oxygen coverage at the grain boundaries from 1.2 to 0.9 monolayers resulted in an increase in leakage current at 1 V/mm by about 7 orders of magnitude! This shows the strategic role played by the boundary chemistry in insuring optimum properties, homogeneity and reproducibility. At MIT, the following approach is being taken: (1) prepare electrically active boundaries with considerably simplified chemistry compared to commercial devices, and (2) systematically modify the chemistry of selected

boundaries by in-diffusion of cation dopants and/or oxygen.

In the first approach, samples investigated originated from studies by Lee and Chiang [11–13] of Bi segregation in ZnO as a function of composition, microstructure, pressure and thermal history. Samples, hot-pressed from co-precipitated Bi and Co doped powders, were shown by scanning transmission microscopy (STEM) to segregate only Bi and that the level and uniformity of segregation was controllable. Figure 5 illustrates the variation in Bi segregation with heat treatment. Specimens initially fired at 850, 1000 and 1150°C without post annealing at 700°C, show a broad distribution in bismuth segregation from boundary to boundary. Following a 700°C post anneal, resulting in dewetting of the boundaries by

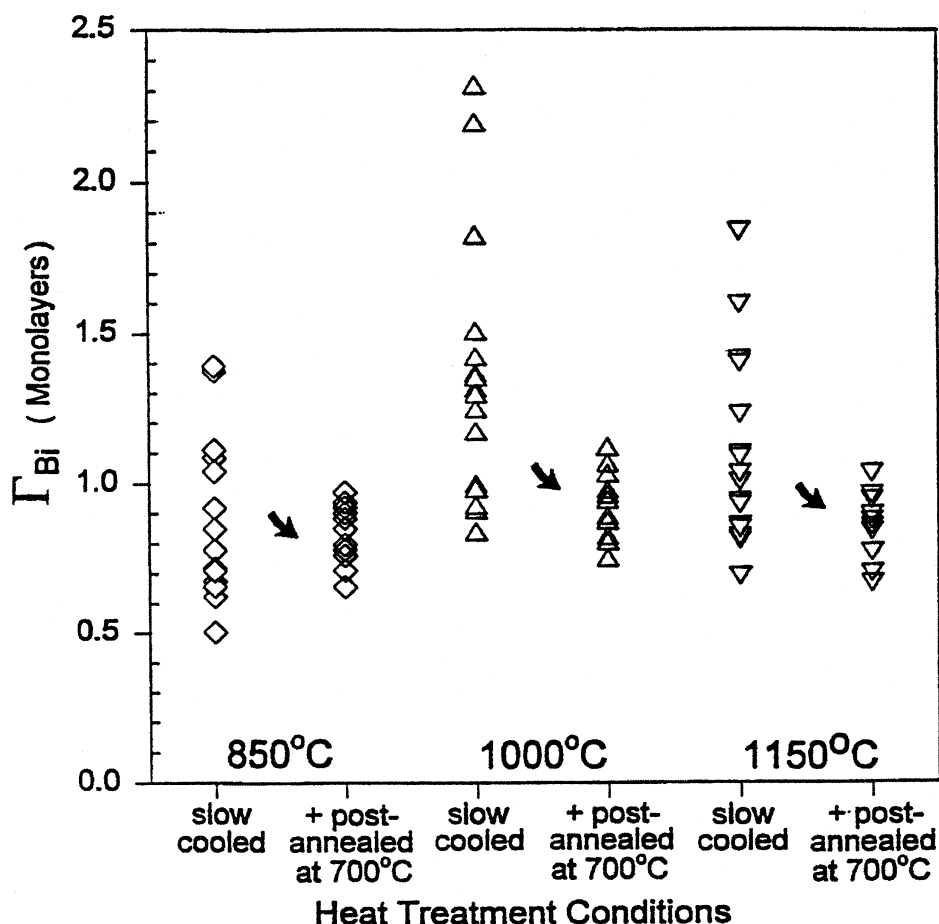


Fig. 5. Variation of bismuth grain boundary coverage  $\Gamma_{Bi}$  before and after post annealing treatment following different initial treatment temperatures. Samples were initially fired at 850, 1000 and 1150 C and slow cooled at 150 C/hr. The post annealing was conducted at 700°C for 24 h and slow cooled thereafter at 150 C. Results from Ref. [12].

the Bi rich phase below the eutectic, a highly uniform segregation with an average coverage of 0.88 monolayers results regardless of grain size.

The  $I$ - $V$  characteristics of specimens with the same thermal histories as the specimens described in Fig. 5 are compared in Fig. 6. A number of features of interest become apparent from these results. First, for the smaller grain size specimens (sintered at the lower temperatures of 850 and 1000°C),  $\alpha$  values as high as the order of 30 are obtained, even when limited to only two additives (Bi and Co). Second, specimens with and without the 700°C post-anneal manifest similar  $I$ - $V$  characteristics, despite having markedly different bismuth segregation distributions. Lastly, one notes the higher leakage currents associated with the larger grain specimens which may reflect uneven oxidation upon cooling and/or higher probabilities for leaky percolation pathways [12]. Deep level transient spectroscopy (DLTS) measurements performed on these specimens showed two shallow bulk levels at  $\sim 0.14$  and  $\sim 0.24$  eV and one interfacial level at  $\sim 1.0$  eV [14] similar to those observed in the more chemically complex commercial varistors [1]. Further, this three-peak signature was present even when the Bi distribution at the grain boundaries was dramatically changed.

In the second approach, Tuller and Baek [10] applied the SID method with the large dopant limited to Pr and transition elements selected from the group Mn, Co and Ni in order to systematically investigate the role of the specific boundary chemistry. Breakdown voltages as low as  $\sim 3$  volts and  $\alpha$  values as high as 12 were obtained. DLTS studies of these SID samples are summarized in Fig. 7. Surprisingly, the position of the levels appear to be insensitive to the specific transition metal utilized [10]. This suggests that the levels are likely associated with defects in the ZnO lattice with the additives serving to activate these key levels, i.e., shifting their positions in energy or their occupancies such that they serve to trap carriers from the adjacent grains. Further work is necessary to confirm this hypothesis and to identify these active lattice defects.

## Diffusion

Grain boundary diffusion of oxygen determines the kinetics of the preferential boundary oxidation during cooling. Cation diffusion is central to the surface in-

diffusion process as well as the kinetics of cation redistribution at the grain boundaries in commercial devices driven by boundary precipitation and second phase formation. It is therefore essential that we obtain a clearer understanding of the boundary diffusion process. This is hampered in many oxides, including ZnO, since even fundamental questions regarding diffusion in the bulk remain unanswered. These include: (a) the nature of the predominant mobile defect species, (b) whether stoichiometry or dopants control and (c) the relative contributions of formation and migration terms to the measured activation energy. Our studies are directed towards answering these questions for both bulk and boundary diffusion in ZnO.

Preliminary measurements of Co diffusion into ZnO, determined by analyzing in-diffusion profiles by electron microprobe, show it to have a positive dependence on oxygen partial pressure under oxidizing conditions [15]. This surprising result, given that ZnO is normally viewed as being metal excess, would imply, from a defect chemical standpoint, that cation diffusion at 1100°C is via a vacancy mechanism. Consider, for example the oxidation reaction:



which for the approximate neutrality condition:

$$[V'_{\text{Zn}}] = p = K_{\text{ox}}^{1/2}P_{\text{O}_2}^{1/4}$$

Indeed, nearly a  $P_{\text{O}_2}^{1/4}$  dependence of the Co diffusivity was observed [15]. Since both the bulk and grain boundary diffusivities showed similar behavior with respect to  $P_{\text{O}_2}$ , this implies that grain boundary diffusion is also controlled by a similar defect equilibria. Finally, this analysis also points to the fact that the measured activation energy is made up of a formation and a migration term. A detailed analysis of these results will be published shortly [15].

Oxygen diffusion in undoped ZnO single and polycrystals was studied by  $^{18}\text{O}/^{16}\text{O}$  exchange followed by SIMS analyses of the resultant diffusion profiles [16]. Bulk diffusion is characterized by the expression

$$D_{\text{O}}(\text{cm}^2/\text{S}) = 1.42 \times 10^{-5} \exp(-2.84 \text{ eV}/kT)$$

while grain boundary diffusion is given by

$$D'\delta(\text{cm}^3/\text{S}) = 1.62 \times 10^{-7} \exp(-2.90 \text{ eV}/kT)$$

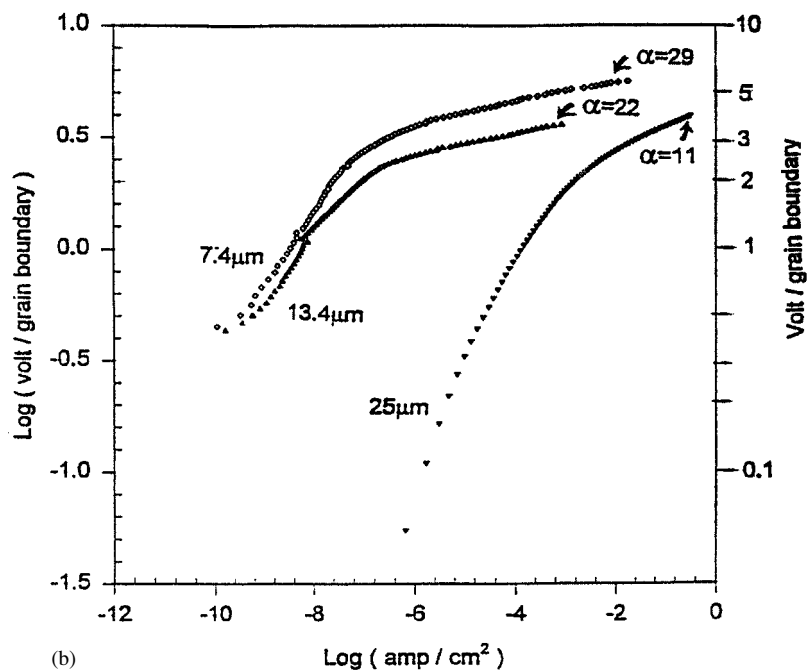
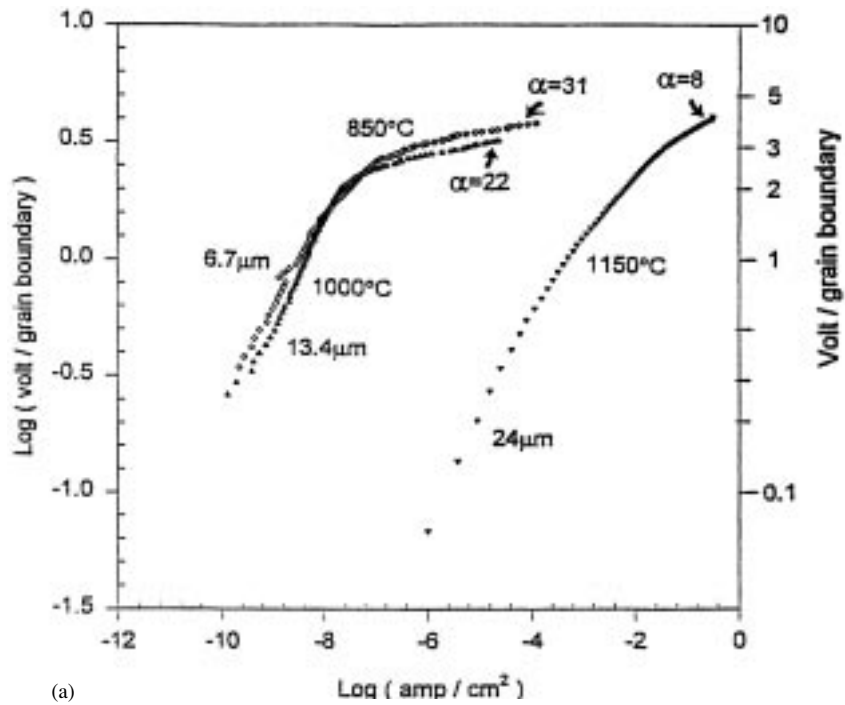


Fig. 6. I-V curves for samples described in Fig. 5. (a) Curves for samples with uninterrupted slow cool and (b) curves for samples with additional 700°C, 24 h post anneal. From Lee [12].

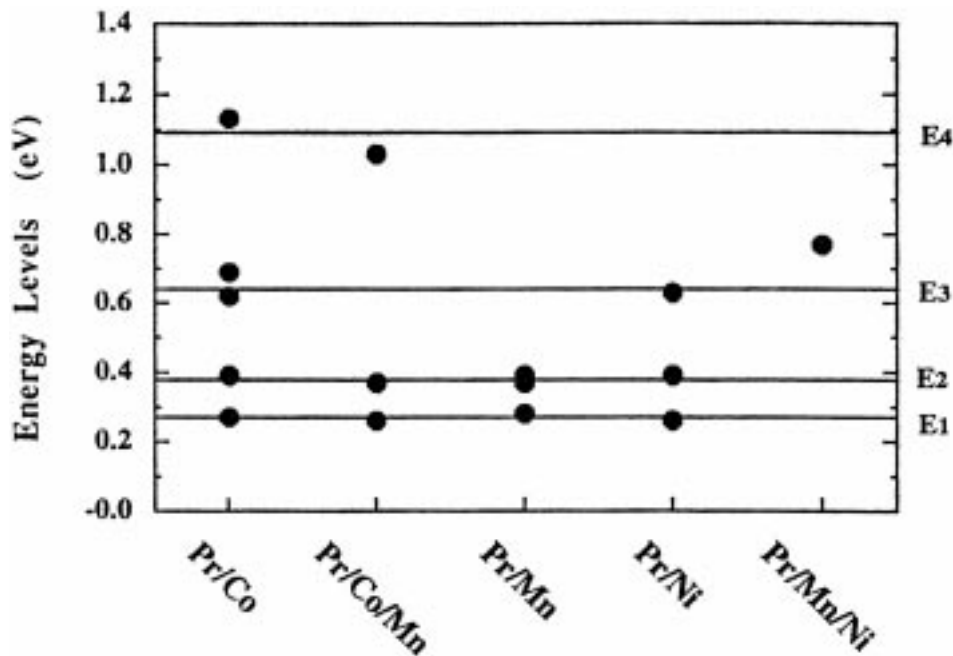


Fig. 7. Trap energy levels obtained from DLTS measurements on SID samples with Pr and different combinations of transition metals at the active interface. E1 and E2 are bulk traps and E3 and E4 are interface states. From Tuller and Baek [10].

The present oxygen grain boundary diffusivities are compared with recent results by Claus et al. [17] and Haneda et al. [18] in Fig. 8. The trapezoidal area indicated for Haneda et al.'s results include data for Li-, Al-, Co- and Mn- and un-doped ZnO specimens. For grain boundary diffusion, no clear trends as a function of additive are apparent. With respect to bulk diffusion, Haneda et al. [18] observe a somewhat stronger trend pointing to  $D_O$  enhancement with Al and depression with Li pointing to an interstitial mechanism.

Assuming, as is commonly done, that the effective boundary width  $\delta$  is 1 nm, then the enhancement factor  $D'/D_O$  is seen to be  $\sim 60,000$  at  $T \sim 1,000^\circ\text{C}$ . Since the activation energies for the two diffusivities are nearly equal, this would suggest that the same process applies to both regions but that the defect density is higher at the boundary, presumably, due to space charge effects [2]. This suggestion requires further confirmation.

### Summary

The operation and performance of electroceramics often depend critically on the characteristics of

electrically active grain boundaries. To date, our understanding of the role of specified additives and heat treatments on the grain boundary properties remains underdeveloped. This can be rectified if efforts are directed towards (a) examining individual boundaries, (b) controlling and simplifying boundary chemistry and (c) systematically investigating properties (e.g.,  $I$ - $V$ , DLTS,  $D_O$  and  $D_M$ ) as a function of boundary structure and chemistry and (d) developing appropriate energy band, defect and diffusion models. Following these approaches, preliminary results suggest that lattice defects play critical roles in controlling both the electrical and diffusive properties of the boundaries. The essential additives and heat treatments appear to act in a supportive manner by "activating" the key lattice defects.

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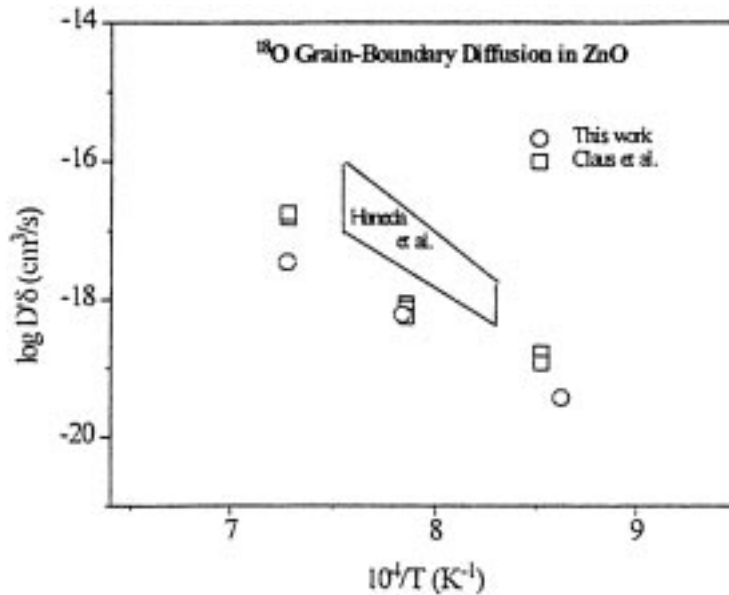


Fig. 8. The product of oxygen grain boundary diffusivity  $D'$  and effective boundary width  $\delta$  in ZnO as a function of reciprocal temperature. From Sabioni et al. [16]. Other data from Claus et al. [17] and Haneda et al. [18].

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## References

1. F. Greuter, G. Blatter, M. Rossinelli, and F. Stucki, in *Ceramic Transactions, Vol. 3, Advances in Varistor Technology*, edited by L. M. Levinson (American Ceramic Society, Westerville, OH, 1988) p. 31.
2. H. L. Tuller, J. Claus, and T. Chen, in *Electroceramics-Proc. Fourth Euro Ceramics, Vol. 5*, edited by G. Gusmano and E. Traversa (Gruppo Edit. Faenza Editrice, Faenza, Italy, 1995) p. 443.
3. M. Tao, B. Ai, O. Dorlance, and A. Loubiere, *J. Appl. Phys.*, **61**, 1562 (1987).
4. J. T. C. van Kemenade and R. K. Eijthoven, *J. Appl. Phys.*, **50**, 938 (1979).
5. G. D. Mahan, L. M. Levinson, and H. R. Philipp, *Appl. Phys. Lett.*, **33**, 830 (1978).
6. E. Olsson and G. L. Dunlop, *J. Appl. Phys.*, **66**, 3666 (1989).
7. R. Einzinger, in *Advances in Ceramics, Vol. 1*, edited by L. M. Levinson and D. C. Hill (American Ceramic Society, Columbus, OH, 1981) p. 359.
8. U. Schwing and B. Hoffmann, *J. Appl. Phys.*, **57**, 5372 (1985).
9. M. H. Sukkar and H. L. Tuller, in *Nonstoichiometric Compounds—Surfaces, Grain Boundaries and Structural Defects*, edited by J. Nowotny and W. Weppner (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1989) p. 237.
10. H. L. Tuller and K. K. Baek, in *Grain Boundaries and Interfacial Phenomena in Electronic Ceramics*, edited by L. Levinson (American Ceramic Society, Columbus, OH, 1993) p. 19.
11. J.-R. Lee and Y.-M. Chiang, *Solid State Ionics*, **75**, 79 (1995).
12. J.-R. Lee, PhD Thesis, Department of Materials Science and Engineering, (Massachusetts Institute of Technology, 1995).
13. J.-R. Lee and Y.-M. Chiang, *iib'95, Proc. Int. Conf. On Intergranular and Interphase Boundaries* (Lisbon, Portugal, June, 1995).
14. T. D. Chen, J.-R. Lee, H. L. Tuller, and Y.-M. Chiang, *MRS Proc. Vol. 411*, (Materials Research Society, Pittsburgh, PA, 1996), p. 295.
15. J. Claus, H. L. Tuller, and B. J. Wuensch, *Lattice and Grain Boundary Diffusion of Metal Dopants in ZnO*, in preparation.
16. A. C. S. Sabioni, H. L. Tuller, and B. J. Wuensch, *Oxygen Diffusion in ZnO Polycrystals*, in preparation.
17. J. Claus, H. L. Tuller, and B. J. Wuensch, unpublished.
18. H. Haneda, I. Sakaguchi, A. Watanabe, and J. Tanaka, in *Proc. DIMAT '96* (International Conference on Diffusion in Materials), edited by H. Mehrer, Nordkirchen, Germany, 5–9 August 1996, in press.