

PII: S1359-6454(96)00235-2

PRESSURE-THERMODYNAMIC STUDY OF GRAIN BOUNDARIES: Bi SEGREGATION IN ZnO

J.-R. LEE, Y.-M. CHIANG and G. CEDER

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

(Received 6 November 1995; accepted 9 April 1996)

Abstract—A pressure-thermodynamic study of solid interfaces (grain boundaries) has been conducted. The influence of a high quasi-hydrostatic pressure (~1 GPa) on interfacial segregation of Bi in ZnO has been characterized. At ambient pressure (1 atm) and sub-eutectic temperatures, grain boundaries in Bi-saturated ZnO exhibit near-monolayer levels of Bi segregation characterized by a segregation enthalpy of ~0.67 eV/atom. Under ~1 GPa pressure, however, the segregation is nearly completely suppressed. The segregation and pressure-induced de-segregation are highly reversible, with the source/sink for Bi being a Bi-rich secondary phase located at multiple grain junctions. The secondary phase serves as a reference of known molar volume, from which it is determined that the partial molar volume of Bi₂O₃. The greater specific volume due to Bi segregation may be associated with charge-compensating point defects important in creating interface electronic states, and may facilitate rapid grain boundary oxidation in ZnO varistors. *Copyright © 1997 Acta Metallurgica Inc.*

1. INTRODUCTION

The atomic disorder and excess volume associated with many solid-solid interfaces, including grain boundaries, suggests that pressure should have a larger influence on phase equilibria and physical properties of interfaces than of bulk phases. However, the influence of pressure on interfacial phenomena has not been widely studied, and for grain boundaries, the primary effect studied is that of pressure on diffusion [1]. Recently a significant effect of pressure on liquid wetting of grain boundaries in the Fe-Si-Zn has been reported [2], which gives an indication of the difference in excess volume for solid-solid and solid-liquid interfaces. In the present study, we show that solute segregation at grain boundaries in solid-state equilibrium can have a large pressure dependence. When an appropriate internal reference phase is available, these results can be analyzed to determine the partial molar volume of the segregating component at grain boundaries. The results have specific implications for electrical properties of the zinc oxide system which is studied, and more broadly suggest that pressure-thermodynamics studies may have an important and previously overlooked role in understanding the structure, phase transformations, and related properties of solid interfaces.

The system examined in this work is zinc oxide doped with bismuth oxide, which represents the simplest composition in which varistor behavior (highly nonlinear current-voltage characteristics) is found, and is a model for electrically active grain

boundaries in semiconducting oxides. The phase diagram for the ZnO-Bi₂O₃ system (Fig. 1) shows a single eutectic at 740°C below which zinc oxide coexists with either α -Bi₂O₃ (in metastable equilibrium) or 24Bi₂O₃:ZnO (at equilibrium). In equilibrium with either solid phase, zinc oxide has a very low solubility for bismuth oxide (<0.023mole%) [3], and exhibits strong segregation of Bi to grain boundaries [4, 5]. In order to obtain grain boundary electrical barriers giving rise to nonlinear conduction, the segregation of Bi as well as an oxidative cooling cycle after high temperature firing are required [5-7]. While the importance of Bi segregation has long been recognized, the specific role of Bi in creating interface electronic states associated with varistor activity, and the physical identity of the interface states, remains unknown. The processing of polycrystalline varistors is complex and involves liquid-phase sintering at temperatures well above the eutectic, followed by slow cooling, during which various microstructural changes take place. The work reported here focuses on subsolidus segregation behavior; grain boundary segregation in solid-liquid equilibrium is discussed in Ref. [8], and the relationship between processing, segregation, and electrical properties is discussed in Ref. [3]. A short report of the present work appeared as Ref. [9].

2. EXPERIMENTS

Chemically derived, homogeneous ZnO powders doped with Bi_2O_3 or $Bi_2O_3 + CoO$ were prepared as described in Ref. [8]. Compositions were analyzed



Fig. 1. Equilibrium phase diagram for ZnO-Bi₂O₃, from Ref. [17]. Rapid quenching of Bi₂O₃-rich melts frequently permits α -Bi₂O₃ to be retained as a metastable phase.

by inductively-coupled plasma emission spectroscopy (ICP); all compositions given below are actual analyzed concentrations. The starting powders were densified to greater than 95% of the theoretical density, and subjected to pressure experiments at sub-eutectic temperatures ($\sim 650^{\circ}$ C) in a tungsten carbide piston-anvil apparatus with a bore of 0.25 in. All experiments were conducted in air, although the local environment within the apparatus is likely to be more reducing. The time and temperature of the experiments were varied as discussed below, and following each experiment the sample was rapidly cooled within the die, then removed for scanning transmission electron microscopy (STEM) measurements using either a Fisons/Vacuum Generators HB5 or HB603 instrument. In both instruments a Link Systems thin-window energy dispersive X-ray detector was used to determine concentration. A specially prepared ZnO-Bi₂O₃-SiO₂ glass of analyzed Bi/Zn ratio (by ICP) was used as the calibration standard in both instruments. Segregation results are presented in terms of grain boundary Bi coverage, $\Gamma_{\rm Bi}$, given in monolayer equivalents relative to the Bi cation site density $(N_{\rm Bi})$ in δ -Bi₂O₃, wherein one monolayer is equal to $(N_{\rm Bi})^{2/3} = 8 \times 10^{14} \,{\rm cm}^{-2}$ This reference lattice is chosen solely for consistency with related work [3] and alternatives such as the Zn site density in ZnO may also be used [8], wherein one monolayer is equivalent to $1.2 \times 10^{15} \text{ cm}^{-2}$. The method of measuring the grain boundary coverage is that of Ikeda et al. [9], wherein a volume of the thin foil containing the grain boundary is defined by the rastered STEM beam and the excess solute per unit area is obtained using similar analyses in the adjacent grains as a reference. The details are described elsewhere [3, 8, 10]. The detection limit varies depending on the volume analyzed, the X-ray collection time, and the solute of interest. In the present study, the detection limit for Bi segregation

is approximately 0.02 monolayers $(1.6 \times 10^{13} \text{ cm}^{-2})$. The Bi-rich secondary phase co-existing with ZnO during these experiments was characterized using X-ray diffraction, in samples containing sufficient secondary phase for it to be readily identifiable.

3. RESULTS

3.1. Bi segregation at ambient pressure (1 atm)

When varistors were first introduced by Matsuoka [11] in 1971, he suggested that a Bi-rich segregation layer at ZnO grain boundaries was responsible for the non-ohmic properties. Segregation of Bi was subsequently confirmed by Kingery et al. [4], and semi-quantitative estimates of the Bi concentration at grain boundaries have ranged from 0.5 to 1 monolayer [5, 6]. Using the present STEM techniques, Lee and Chiang [3, 8] more precisely quantified both the coverage and its variation from grain boundary to grain boundary. Above the eutectic temperature, the Bi coverage ranges from one to several monolayers, and can be discussed in the context of thin liquid films under capillary pressure (much lower pressures than those applied here) [3].

Of greater importance for the pressure experiments discussed below is the equilibrium segregation of Bi at sub-eutectic temperatures and ambient pressure. Figure 2 shows $\Gamma_{\rm Bi}$ measured at a number of grain boundaries in a sample containing 0.023 mole% Bi₂O₃, equilibrated at 725°C. The variation in coverage between boundaries is small, with the average value of $\Gamma_{\rm Bi}$ being 0.48 monolayers. A uniform level of Bi segregation is characteristic of grain boundaries in solid-state-equilibrated ZnO polycrystals. No crystallographic texture, which might result in similar grain boundary structures, is apparent in the samples we have examined. The doping level of the sample represented by Fig. 2 is within the solid solution limit, and no Bi-rich secondary phase was observed by STEM and HREM. However, most of the compositions we



Fig. 2. Bismuth coverage, Γ_{Bi} , in monolayers relative to the crystal density of δ -Bi₂O₃, measured at a number of grain boundaries in polycrystalline ZnO containing 0.023 mol% Bi₂O₃, equilibrated at 725°C. The results represent equilibrium segregation of Bi at concentrations below the saturation limit for this system of ~0.9 monolayers (see Fig. 3).

1249

studied exceeded the solubility limit, in which case saturation of the available number of grain boundary sites becomes a possibility, and the temperature dependence of segregation includes changes in the lattice solubility of Bi. Figure 3 shows the measures Γ_{Bi} as a function of the Bi₂O₃ doping level for polycrystalline samples equilibrated for long times (>12 h) at 700°C. Each datum represents a single grain boundary in a polycrystal, while the filled circles are the mean values of coverage. The average coverage increases with doping level, reaching a plateau value higher than that in Fig. 2. This is consistent with the fact that the doping level of the sample in Fig. 2 is below the solubility limit. The results further show that there exists a saturation level for Bi segregation at ZnO grain boundaries of approximately 1 monolayer with respect to δ -Bi₂O₃ (0.67 monolayer with respect to ZnO). While grain boundary saturation is reached at a low bulk concentration of ~0.06% Bi₂O₃, this alone does not prove that the solid solution limit at 700°C has been exceeded, since for strong adsorption the available number grain boundary sites can be filled before the solid solution limit is reached. However, using STEM [3] we have observed Bi-rich secondary phases in samples containing 0.06% Bi2O3 annealed near the eutectic temperature, while none were seen in the sample containing 0.023% Bi₂O₃. The maximum solid solubility of Bi₂O₃ in ZnO appears to lie between 0.023 and 0.06% Bi₂O₃, contrary to previous reports of solubilities as high as 0.21% at 750°C [12].

The results in Fig. 2 can be analyzed as Langmuir adsorption at the grain boundary below the saturation level. For segregation of a single atomic specie in a single layer, with no site-to-site



Fig. 3. Bi coverage (Γ_{Bi}) as a function of doping level in polycrystalline ZnO samples equilibrated at 700°C. Each open datum represents a measurement from one grain boundary, while the filled circles are the mean values. Γ_{Bi} increases with the bulk doping level, reaching saturation at about 0.9 monolayers.

interactions and a fixed number of adsorption sites, the concentration of segregant at the grain boundary, x_{s} , can be expressed by McLean's result [13]:

$$\frac{x_{\rm s}}{x_{\rm So} - x_{\rm s}} = \frac{x_{\rm bulk}}{1 - x_{\rm bulk}} \exp\left(\frac{H_{\rm s}}{kT}\right) \tag{1}$$

in which x_{so} is the saturation level of x_s , x_{bulk} is the bulk concentration of Bi, and H_s is the adsorption enthalpy, representing the difference between Bi at a grain boundary site and at a lattice site. Using an average saturation level of $x_{so} \sim 0.9$ monolayers, as shown by Fig. 3, an adsorption enthalpy of $H_s = 65 \text{ kJ/mol} (0.67 \text{ eV/atom})$ is obtained for the results in Fig. 2 (sample containing 460 ppm Bi). Notice that H_s can only be obtained from results for samples in which segregation has not reached the saturation level.

Due to the large difference in ionic radius between bismuth and zinc $R(Bi^{3+}) = 0.120$ nm; $R(Zn^{2+}) =$ 0.074 nm), it is likely that substitution of bismuth for zinc in the lattice results in a misfit strain energy which contributes to the driving force for segregation. The simplest estimate of the strain energy, certainly incorrect in detail, assumes a homogeneous elastic sphere in an elastic matrix:

$$E_{\rm s} = \frac{24\pi KGr_{\rm s}r_{\rm b}(r_{\rm s}-r_{\rm b})^2}{4Gr_{\rm b}+3Kr_{\rm s}}$$
(2)

where K is the bulk modulus of the solute, G is the shear modulus of the matrix, and r_{s} and r_{b} are the radii of the solute and solvent respectively. Moduli are available for ZnO [14], but not for Bi₂O₃. Since the bulk modulus of Bi₂O₃ should clearly be lower than that of ZnO, we somewhat arbitrarily assume it to have half the ZnO value. Using $G_{ZnO} = 45.5$ GPa and $K_{\text{Bi}_2\text{O}_3} = K_{\text{ZnO}}/2 = 72 \text{ GPa}$ [14] in equation (2), we obtain $E_s = 71 \text{ kJ/mole}$, in surprisingly good agreement with the experimental value. Additional chemical or electrostatic [10] driving forces for segregation may well exist that are not included in the estimate, and the strain energy itself may not be completely relieved upon segregation. The principle conclusion of importance for comparison with the following pressure-desegregation results is that Bi has a sufficiently large segregation enthalpy that in all samples where the solid solubility has been exceeded, the equilibrium grain boundary coverage (in the absence of wetting liquid phases) reaches a saturated value of nearly 1 monolayer).

3.2. Effect of pressure on segregation

All of the samples used for pressure-segregation experiments contained Bi_2O_3 in excess of the solid solution limit. The secondary phase in equilibrium with ZnO varied depending on the composition and method of sample preparation, and included BiOCl, α -Bi₂O₃, and 24Bi₂O₃:ZnO. The oxychloride phase results from residual chlorine is left by the chloride starting materials used in powder preparation, and is retained only if the sample is processed under 700°C and in a closed environment such as the hot-pressing die [3]. Under normal open firing conditions the BiOCl decomposes at temperatures between 700 and 750°C, losing Cl by vaporization and leaving behind either $24Bi_2O_3$:ZnO or α -Bi₂O₃ as the secondary phase. At the temperature of the pressure experiments, all of these secondary phases form highly dispersed, non-wetting precipitates located primarily at grain boundaries and three- or four-grain junctions, and occasionally within grains. Experiments were conducted both in the absence of any transformation in the secondary phase, as well as with a pressure-induced transformation from 24Bi₂O₃:ZnO to α -Bi₂O₃. The former phase appears to be isostructural with γ -Bi₂O₃ [15], while the latter is the highest density polymorph of bismuth oxide [16].

Equilibration with BiOCl secondary phase. We first illustrate the effects of applied pressure on Bi segregation using results from a series of four experiments conducted on a sample doped with 0.23% Bi₂O₃, and in which X-ray diffraction showed the secondary phase to be BiOCl both before and after thermal equilibration under 1 GPa pressure. In Fig. 4 the pressure-time cycles of each experiment are illustrated at the left, and the Γ_{Bi} values measured at a number of randomly selected grain boundaries in a polycrystal are shown in the histograms at the right. In the first instance (a), the starting powder was densified under 1 GPa pressure for 2 h, after which the sample was completely dense and had a grain size of 2–3 μ m. Virtually no Bi segregation is detected. A



Fig. 4. Pressure-segregation experiments at 650°C in ZnO + 0.23% Bi₂O₃. In each experiment (a-d) the pressure-time cycle is indicated at the left, while the resulting segregation measured at a number of polycrystalline boundaries is indicated in the histogram at the right.

second experiment (b), subjected the sample to 1 GPa pressure for 12 h, in order to allow additional Bi atom diffusion and grain coarsening (to a final grain size of $\sim 5 \,\mu$ m). The corresponding STEM analyses again show virtually no detectable segregation (mean value less than 0.02 monolayer).

In a third experiment (c), the sample was first densified as above, and then the pressure was released and the sample annealed for an additional 10 h at ambient pressure. The corresponding STEM results show a high level of segregation at all boundaries, with an average $\Gamma_{\rm Bi}$ of 0.71 monolayer, and little



Fig. 5. Microstructure (fracture surface) of a sample representative of experiments in Fig. 4. After hot-pressing at 1 GPa pressure at 650°C for 2 h, dispersed non-wetting particles of BiOCl are observed at grain boundaries and multiple grain junctions.

boundary-to-boundary variation. The coverage is slightly less than the equilibrium level shown in Fig. 2, for reasons discussed later, but is otherwise in agreement with results for equilibrium segregation under one atmosphere pressure.

In the fourth experiment (d), the thermal cycle of experiment (c) was repeated, following which the sample (now with 0.7 monolayer segregation coverage) was again subjected to 1 GPa applied pressure for 2 h. Nearly complete *de-segregation* of Bi was observed. This result shows that the influence of applied pressure on segregation is reversible, and is not the result of insufficiently fast atom diffusion kinetics.

Figure 5 shows the highly dispersed, discrete precipitates of BiOCl in this sample. The slightly lower equilibrium value of Γ_{Bi} in Fig. 4(c) has also been observed [3] for samples processed in open environment, but at lower temperatures, such that chlorine is retained. It was observed that as the chlorine is removed by higher temperature firing, $\Gamma_{\rm Bi}$ systematically increases. One possible explanation is that the lattice solubility (chemical potential) of Bi is lowered when the equilibrium secondary phase is BiOCl rather than Bi_2O_3 , which would mean that the grain boundaries in Fig. 4(c) are not fully saturated. A more likely explanation is that the saturation level of $\Gamma_{\rm Bi}$ is lower when chlorine is present, due to a negative co-segregation interaction between Bi substituted for Zn (in Kröger-Vink notation, Bizn) and Cl substituted for O (Clo), each of which have a +1 effective charge as point defects. Due to a strong peak overlap between the Cl K α line (2.62 keV) and the Bi M β line (2.53 eV), any segregation of Cl to grain boundaries is difficult to detect when there is significant Bi segregation. In samples where the Bi segregation has been completely suppressed by pressure, we did observe segregation of Cl at concentrations of ~ 0.2 monolayers [3].

With simultaneous transformation in the secondary phase $(24Bi_2O_3:ZnO \ to \ \alpha-Bi_2O_3)$. Additional experiments were conducted on samples first fired above the eutectic temperature (i.e. at 850°C), whereupon Cl evaporates and leaves only oxide phases. The Bi-rich liquid is initially continuous along three-grain junctions, and crystallizes upon cooling to leave the equilibrium 24Bi₂O₃:ZnO phase (Fig. 6(a)). When these samples were subsequently annealed under 1 GPa applied pressure at 650°C, the continuous phase dewets the grain junctions, forming discrete particulates. Simultaneously, the de-segregation of Bi was again observed. Two particular compositions were examined. Figure 7 compares the segregation observed in a sample containing 0.4 mol% Bi₂O₃ + 0.6 mol% CoO (also used in our varistor studies) after slow cooling from 850°C, with that seen after subsequently applying 1 GPa pressure for 2 h at 650°C. Nearly complete desegregation is again observed. The Co is primarily a lattice dopant in ZnO and does not segregate in detachable concentrations in the present samples; its accumulation at grain boundaries, if any, is less than ~0.05 monolayers.†

Figure 8 shows similar behavior in a sample doped with Bi₂O₃ alone (0.23 mole %). At ambient pressure, $\Gamma_{\rm Bi}$ measurements in three different samples: (a) slowly cooled from 850°C; (b) and (c), subsequently annealed for 24 h at 600 and 700°C, respectively, all show essentially saturated coverage. When a slowcooled sample was annealed under 1 GPa pressure for 2 h at 650°C, the coverage decreased substantially, as shown in Fig. 8(d). However, the residual Bi coverage is higher than in Fig. 7, with an average $\Gamma_{\rm bi}$ value of 0.34 monolayers. The reason for this higher coverage is not known, but we do not believe it to be related to Co doping. A possible explanation is that the internal pressure within the die in the second case was somewhat lower than that applied, due for example to die-wall friction. Further experiments are required to substantiate this hypothesis. The thin-disc samples were sectioned for STEM in an orientation such that the grain boundaries characterized are oriented approximately parallel to the pressing direction. We have examined in one sample grain boundaries oriented both parallel and normal to the pressing direction, but discerned no difference in segregation between the two orientations in that case, both being fully desegregated.

During the pressure-desegregation treatment of the sample in Fig. 8(d), the grain size increased from $\sim 5 \,\mu\text{m}$ to $\sim 9 \,\mu\text{m}$ (Fig. 6), which is a much more rapid rate of grain growth than seen in samples annealed in ambient pressure at the same temperature. All pressure-desegregated samples exhibited accelerated grain growth, which we attribute to a higher grain boundary mobility for grain boundaries without Bi segregation, i.e. lower solute-drag.

In the samples represented by Figs 7 and 8, X-ray diffraction showed that the secondary phase had transformed from $24Bi_2O_3$:ZnO to α -Bi₂O₃ during the pressure-desegregation treatment. The stabilization of the latter under pressure is not surprising when we consider the change in molar volume. α -Bi₂O₃ and ZnO have molar volumes of 49.73 cm³ [16] and 14.52 cm³, respectively, while $24Bi_2O_3$:ZnO phase has a molar volume (normalized by dividing by 25) of 53.26 cm³ [17]. Decomposition of $24Bi_2O_3$:ZnO to α -Bi₂O₃ and ZnO in the stoichiometric ratio, therefore, results in a decrease in molar volume of about 9%.

Given the pressure-induced phase transformation, results under ambient pressure (Fig. 8(b) and (c)) reflect Bi segregation in equilibrium with 24Bi₂O₃:ZnO, while the results under 1 GPa pressure,

[†]This is not to say that Co *never* segregates to grain boundaries in ZnO. Electric field-driven segregation of Co has previously been reported by Chiang *et al* [18], and in commercial varistor compositions, we have also seen Co segregation in conjunction with other dopants.



Fig. 6. (A) Samples cooled from above the eutectic temperature contain a continuous network of 24Bi₂O₃:ZnO located at three-grain junctions that is a crystallization product of the Bi₂O₃-rich liquid;
(B) Annealing below the eutectic temperature (650C, 1 GPA) causes dewetting of the grain junction phase and simultaneously a transformation to α-Bi₂O₃.

Figs 7(b) and 8(d), are at least partially equilibrated with α -Bi₂O₃. The impact of this phase transformation of the interpretation is minor, as discussed later. Nonetheless, since the final reference phase is α -Bi₂O₃, in order to evaluate the magnitude of the pressure effect it is desirable to know the segregation level for equilibrium with α -Bi₂O₃ at ambient pressure. Due to the difficulty of preserving this metastable phase at one atmosphere pressure, an unequivocal measurement was not possible. However, on thermodynamic grounds alone, it can be argued that Γ_{Bi} will also be saturated in this instance. Since the activity of Bi in metastable equilibrium with α -Bi₂O₃ must be elevated in comparison with that defined by the equilibrium phase 24Bi₂O₃:ZnO, a higher Bi lattice solubility and correspondingly



Grain Boundary

Fig. 7. Pressure-induced desegregation in ZnO + 0.4 mol% Bi₂O₃ + 0.6 mol% CoO. (a) Bi segregation after slow cooling from above the eutectic temperature. (b) Nearly complete desegregation observed after application of 1 GPa pressure at 650°C. Concurrently, the secondary phase has transformed from 24Bi₂O₃:ZnO to α -Bi₂O₃.

greater (or saturated) equilibrium segregation must result for the same adsorption energy (cf. equation (1)).

 α -Bi₂O₃ secondary phase. We did retain α -Bi₂O₃ as a metastable secondary phase by infiltrating a ZnO polycrystal with Bi₂O₃-rich liquid and rapidly quenching. A hot-pressed Bi-doped sample was first annealed at 850°C in air for 30 min, then immersed in a liquid consisting of 70 mol% Bi₂O₃ + 30 mol% ZnO composition for another 30 min, then airquenched. The infiltrated sample was removed from the excess melt and hot-pressed at 650°C and 1 GPa nominal pressure for 2 h. X-ray diffraction showed that the secondary phase was α -Bi₂O₃ both before and after hot-pressing.

The Bi coverage before hot-pressing is shown in Fig. 9(a). The high average value of Γ_{Bi} (1.24 monolayers) and large variation between boundaries is characteristic of boundary coverages when equilibrated with a partially wetting liquid phase in the absence of capillary pressure, as documented in Ref. [3]. After application of pressure, desegregation was again observed. The residual coverage was higher than in the previous cases at ~ 0.54 monolayers, but is still lower than the saturation value. The higher residual $\Gamma_{\rm Bi}$ may be due to incomplete equilibration after 2 h at 650°C, since the initial Γ_{Bi} is higher and the grain size larger ($\sim 10 \ \mu m$). The internal pressure may also have been less uniform than in the previous experiments, since the sample could not be cut exactly to die dimensions after liquid infiltration and underwent extensive plastic deformation, demonstrated by extensive dislocation networks within ZnO grains, Fig. 10, which were not observed in the other samples.

To summarize the observations, we list in Table 1 the results for the four different compositions studied. In two cases there is a phase change under pressure from $24Bi_2O_3$:ZnO to α -Bi₂O₃, while in the other two, the phase is unchanged. The average Γ_{B_1} remaining after pressure-annealing varies from barely detectable values to ~0.54 monolayers, but is in all instances less than the equilibrium value at ambient atmospheric pressure.

4. PRESSURE-THERMODYNAMIC ANALYSIS

Although the lattice diffusion coefficient of Bi in ZnO has not to our knowledge been measured, at 650°C it is likely very low, and the ZnO grains probably do not equilibrate in the times of the experiments. On the other hand, the microstructures show that virtually all grain boundaries are located in



Fig. 8. Equilibrium segregation and pressure-desegregation in ZnO + 0.23 mol % Bi₂O₃. (a) exhibits the segregation after slow cooling, while (b) and (c) show the equilibrium segregation levels at 600 and 700°C, respectively. Results in (d) show the pressure-induced desegregation at 650°C. Concurrently, the secondary phase has transformed from $24Bi_2O_3$:ZnO to α -Bi₂O₃.



Grain Boundary

Fig. 9. Pressure-desegregation without concurrent phase transformation. ZnO-saturated Bi_2O_3 liquid was used to infiltrate polycrystalline ZnO, resulting in α -Bi₂O₃ secondary phase. (a) shows the segregation measured after air-quenching from solid-liquid equilibrium at 850°C; (b) shows partial desegregation after application of 1 GPa pressure at 650°C.

close proximity to a secondary phase precipitate. It is therefore likely that the secondary phases are the sources and sinks for Bi during pressure desegregation, with the transport of Bi occurring by grain boundary diffusion, as illustrated in Fig. 11[†]. For evaluation of the pressure effect, the secondary phases provide a useful internal reference of known molar volume.

We analyze the pressure dependence of Bi segregation by considering the equilibrium between

the grain boundary and the Bi-rich phase. It is assumed that Bi maintains a stoichiometry of Bi₂O₃ (i.e. fixed 3 + valence) everywhere. Diffusive transport of Bi between the two phases when pressure is applied reflects the existence of a gradient in the Bi₂O₃ chemical potential, $\mu_{Bi_2O_3}$. This gradient can be evaluated by taking the total pressure derivative of $\mu_{Bi_2O_3}$ at a constant temperature:

$$\frac{\mathrm{d}\mu_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}{\mathrm{d}P} = \left(\frac{\partial\mu_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}{\partial P}\right)_{X_{\mathrm{Bi}_{2}\mathrm{O}_{3}}} + \left(\frac{\partial\mu_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}{\partial X_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}\right)_{P} \frac{\mathrm{d}X_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}{\mathrm{d}P} \quad (3)$$

where $(\partial \mu_{Bi_2O_3}/\partial P) = \overline{V}_{Bi_2O_3}$ is the partial molar volume and $dx_{Bi_2O_3}/dP$ is the pressure derivative of Bi_2O_3 concentration in the phase in question.

Equilibrium under pressure between the secondary phase, denoted α , and the grain boundary, denoted β ,

†The rate of recovery of segregation after pressure-induced desegregation provides an estimate of the grain boundary diffusion coefficient. When the de-segregated sample shown in Fig. 8(d) was annealed at ambient pressure at 720°C (20°C below the eutectic) for just 10 min, $\Gamma_{\rm Bi}$ had returned to the equilibrium value. From the mean half-spacing between precipitates of $\sim 1 \, \mu m$, the grain boundary diffusion coefficient $D \sim x^2/t$ is deduced to be greater than $1.7 \times 10^{-11} \text{ cm}^2/\text{s}$ at 720°C. This coefficient is for ambipolar diffusion, since transport of Bi3+ requires the simultaneous parallel transport of O^{2-} if charge neutrality and stoichiometry are to be maintained. The well-documented [5-7] preferential oxidation of grain boundaries during cooling of ZnO varistors suggests that oxygen diffusion along the boundaries is fast, and we argue later that it may in fact be facilitated by the segregation of Bi. It therefore is likely that Bi is the rate-limiting specie dominating the ambipolar diffusion coefficient.



Fig. 10. Microstructure of sample in Fig. 9(b), showing non-wetting α-Bi₂O₃ secondary phase and extensive plastic deformation. VG 603 bright field STEM image.



Fig. 11. Schematic of pressure-segregation experimental configuration. A non-wetting Bi₂O₃-rich phase acts as the source and sink of Bi in equilibrium with the grain boundary. Rapid diffusion of Bi along the boundary facilitates equilibrium under pressure.

requires that the chemical potential for Bi_2O_3 remains equal in the two phases:

$$\bar{V}^{\beta}_{\mathrm{Bi}_{2}\mathrm{O}_{3}} + \left(\frac{\partial \mu^{\beta}_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}{\partial X_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}\right)_{\mathrm{p}} \left(\frac{\mathrm{d}X^{\beta}_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}{\mathrm{d}P}\right)$$
$$= \bar{V}^{\alpha}_{\mathrm{Bi}_{2}\mathrm{O}_{3}} + \left(\frac{\partial \mu^{\alpha}_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}{\partial X_{\mathrm{Bi}_{2}\mathrm{O}_{2}}}\right)_{P} \left(\frac{\mathrm{d}X^{\alpha}_{\mathrm{Bi}_{2}\mathrm{O}_{3}}}{\mathrm{d}P}\right). \tag{4}$$

For pure α -Bi₂O₃ or any secondary phase of fixed composition, the second term on the right-hand side is negligible. Rearranging and integrating between the zero-pressure and pressurized state we obtain:

$$\left(\bar{V}_{B_{i_2}O_3}^{\alpha} - \bar{V}_{B_{i_2}O_3}^{\beta} \right) \cdot P_{appl}$$
$$= \int_{x_{B_{i_2}O_3}^{x_{B_{i_2}O_3}^{\beta}(P = P_{Appl})} \left(\frac{\partial \mu_{B_{i_2}O_3}^{\beta}}{\partial X_{B_{i_2}O_3}} \right)_P dx. \quad (5)$$

The right-hand side of equation (5) and the partial molar volume are assumed to be independent of pressure in this integration. This assumption is justified later. The integral on the right-hand side represents the change in chemical potential due to compositional changes at the grain boundary at constant pressure. Without knowledge of the detailed structure of Bi_2O_3 at the grain boundary it is difficult to evaluate this quantity. Assuming a constant activity coefficient $(a_{Bi_2O_3} = \gamma x_{Bi_2O_3})$ equation (5) simplifies to

$$\left(\bar{V}_{B_{2}O_{3}}^{\alpha}-\bar{V}_{B_{2}O_{3}}^{\beta}\right)\cdot P_{appl}$$
$$=RT\ln\left[\frac{x_{B_{2}O_{3}}^{\beta}(P=P_{appl})}{x_{B_{2}O_{3}}^{\beta}(P=0)}\right].$$
(6)

Thus the change in Bi_2O_3 segregation under pressure is determined by the *difference* between its partial molar volume as a grain boundary segregant, and that in the secondary phase reservoir. The observed decreases in segregation under pressure qualitatively show that Bi_2O_3 segregated at grain boundaries in ZnO possesses greater partial molar volume, $\vec{V}^{\alpha}_{Bi_1O_3} < \vec{V}^{\beta}_{Bi_2O_3}$, than in the secondary phases.

Quantitative evaluation of $\Delta \vec{V}_{Bi_2O_3}$ requires knowledge of the partial molar volume of Bi_2O_3 in the secondary phase. Of the phases under consideration, this is precisely known only for pure α -Bi₂O₃: $\vec{V}_{Bi_2O_3} =$ 49.73 cm³/mol. However, $\vec{V}_{Bi_2O_3}$ in the 24Bi₂O₃:ZnO phase, which is isostructural with γ -Bi₂O₃, is not likely to vary by more than a few percent from this value. We assume that the molar volume calculated on a per-Bi₂O₃ basis for 24Bi₂O₃:ZnO (53.26 cm³/ mol) represents a reasonable upper bound for $\vec{V}_{Bi_2O_3}$, while the molar volume of γ -Bi₂O₃ (50.15 cm³/mol) is a reasonable lower bound. Therefore $\vec{V}_{Bi_2O_3}$ should be between 1 and 7% greater than it is for α -Bi₂O₃. We assume that $\vec{V}_{Bi_2O_3}$ in BiOCl lies within a similar range.

Using these values as the reference molar volumes, we proceed to evaluate $\Delta \vec{V}_{Bi_2O_3}$ for the experimental results in Table 1. For a change in Γ_{bi} from 0.85 to 0.1 monolayers (e.g. sample 3 in Table 1), it is found that the Bi₂O₃ segregated at grain boundaries possesses 33% greater partial molar volume than it does in pure α -Bi₂O₃: $\Delta \vec{V}_{Bi_2O_3} \approx 0.33 V_{\alpha$ -Bi₂O₃. For sample 1 in Table 1 (in equilibrium with BiOCl), the near-absence of segregation under pressure makes it difficult to evaluate $\Delta \vec{V}_{Bi_2O_3}$ precisely, since the result (equation (7)) diverges as the residual segregation vanishes. Many of the pressure-desegregation boundaries in this sample (Fig. 4(a), (b)) have

Table 1. Results of pressure-segregation experiments in four compositions

Sample	Composition	Secondary phase Before/After	Initial Γ _{Bi} (monolayers)	Final Γ _{Bi} (~1 GPa, 650°C, 2 h)
1	$ZnO + 0.23 mol \% Bi_2O_3$	BiOCI/BiOCI	0.71	~ 0
2	$ZnO + 0.23 mol \% Bi_2O_3$	$24Bi_2O_3$: ZnO/ α -Bi ₂ O ₃	0.82	0.34
3	$ZnO + 0.4 mol \% Bi_2O_3$ + 0.6 mol % CoO	$24Bi_2O_3:ZnO/\alpha-Bi_2O_3$	0.86	0.07
4	ZnO polycrystal equilibrated with Bi ₂ O ₃ liquid	$\alpha - Bi_2O_3/\alpha - Bi_2O_3$	1.24	0.54

undetectable Γ_{Bi} values. Taking the STEM detection limit of ~0.02 monolayers as a bounding value, a 50% greater partial molar volume is indicated for Bi₂O₃ at the grain boundary relative to α -Bi₂O₃. For the two remaining compositions (2 and 4) in Table 1, corresponding values would be less, but are probably not meaningful given some evidence that desegregation has either not reached equilibrium, or that full pressure was not attained.

Implicit in the analysis is an assumption that the partial molar volumes of the individual phases do not vary with pressure (in the absence of a phase transformation). This assumption is justified since volume changes due to bulk compressibility are negligible compared to the magnitude of $\Delta \bar{V}_{B_{i}O_{i}}$. The compressibility of crystalline oxides is of order 100 GPa, and that for ZnO specifically is 144 GPa [14]. The 1 GPa experimental pressure therefore causes $\sim 1\%$ volume compression, which is small compared to the observed differences in partial molar volume. Likewise, the 1-7% change in Bi₂O₃ partial molar volume accompanying the phase transformation from 24Bi₂O₃:ZnO to α -Bi₂O₃ under pressure (e.g. for samples 2 and 3 in Table 1) is small compared to the experimental values of $\Delta \bar{V}_{Bi,O_1}$.

Although our assumption of a constant activity coefficient for Bi₂O₃ in the grain boundary does not affect the qualitative conclusions from these experiments, a concentration dependence of this coefficient will result in a different value of $\Delta \bar{V}_{Bi_2O_3}$. However, given the almost linear dependence of Bi segregation with bulk Bi concentration up to the saturation limit, the coverage-dependence of γ seems small.

5. GENERAL DISCUSSION

It is generally accepted that grain boundaries have a lower density than the corresponding crystals. Representative experimental results for the volume expansion at low Σ boundaries, tabulated by Sutton and Balluffi ([1], p. 353), show expansions normal to the boundary plane of 1×10^{-9} , 2×10^{-9} and 4×10^{-9} cm³/cm² for selected grain boundaries in A1, Ge and NiO, respectively. Assuming the expansion to be accommodated within a single atomic layer at the grain boundary, the increase in molar volume relative to the perfect crystal is 20%, 36% and 76%, respectively. The larger relative expansion in NiO is characteristic of ionic systems.

However, it is emphasized that the present experiments do not give the equivalent volume expansion for pure ZnO grain boundaries. They give instead the partial molar volume of Bi_2O_3 in a two-component grain boundary containing both ZnO and Bi_2O_3 . Since the partial molar volume of the ZnO component is not known, the total volume of the grain boundary cannot be precisely determined. Nonetheless, if we assume that the partial molar volume of ZnO at the boundary is not unduly large or negative, then the molar volume of a Bi-saturated boundary is approximately given by the partial molar quantity, \vec{V}_{Bi,O_1} . The analysis shows that the absolute molar volume of a grain boundary consisting mostly of Bi₂O₃ is at least one-third greater than that of the reference bismuth oxidc-rich phases. The magnitude of this expansion seems reasonable in comparison with the results for special boundaries.

The molar volume expansion of Bi₂O₃ as a grain boundary segregant has special significance for the transport and electrical properties of varistor grain boundaries. Firstly, the Bi₂O₃ polymorphs are already considered to be fairly open, low-density structures. δ -Bi₂O₃ is a well-known fast-ion conductor of oxygen, due to the high intrinsic vacancy concentration. A further increase in the molar volume upon segregation seems certain to result in a higher oxygen grain boundary diffusion coefficient compared to undoped ZnO. Grain boundary oxidation is known to be important for the 'activation' of interface states in varistors, and typically occurs during slow-cooling from firing temperatures. The present results provide strong support for the hypothesis, previously suggested by Greuter [6], that a critical role of Bi segregation in creating electrically-active grain boundaries is to increase the rate of oxygen diffusion along ZnO boundaries.

With respect to the role of bismuth in creating electrically-active defect states, it has long been a mystery how the segregation of Bi³⁺, a donor species in ZnO, can give rise to grain boundary acceptor states. We suggest that the excess volume associated with Bi segregation may be accommodated in the form of point defects that are the true physical origin of interface electronic states. Detailed consideration of the grain boundary electronic structure for given atomic configurations involving Bi are necessary to identify these states, to correlate them with measured deep levels in varistors [19], and to understand the role of oxidation. The present results provide support for the idea that it is a point defect accompanying Bi³⁺ segregation, possibly a charge-compensating zinc vacancy, that is the electrically active interface state.

These hypotheses are unlikely to be confirmed without direct examination of the grain boundary atomic structure with and without bismuth segregation. The uniform response to pressure of the many randomly selected boundaries within a polycrystal shows that the effect is general, and not limited to boundaries of a particular structural type. The differences in atomic-level structure suggested by the results should be distinguishable in HREM experiments and computational models. Whether the transition between desegregated and segregated boundaries have the characteristics of a grain boundary phase transformation may also be answered by additional study.

6. CONCLUSIONS

The pressure-thermodynamics of Bi segregation at grain boundaries in ZnO have been studied. Nearly complete desegregation is observed under ~1 GPa quasi-hydrostatic pressure for grain boundaries which under ambient pressure (1 atm) are saturated with ~1 monolayer Bi segregation. Pressure-induced desegregation is observed at all randomly-selected grain boundaries in a polycrystal, in samples with three different Bi-rich secondary phases, and with and without a simultaneous pressure-induced transformation in the secondary phase. The heat of segregation for Bi at 1 atmosphere pressure has been determined to be ~0.67 eV/atom.

Using the Bi-rich secondary phase as an internal reference of known Bi_2O_3 molar volume, a pressurethermodynamic analysis shows that Bi_2O_3 as a grain boundary segregant possesses one-third to one-half greater partial molar volume than in the pure phase α -Bi₂O₃. Results suggest that ZnO grain boundaries with Bi segregation have a highly open structure, which facilitates grain boundary oxidation and the formation of electrically active grain boundary states in ZnO varistors.

Acknowledgements—This research was supported under the MRSEC Program of the National Science Foundation under award no. DMR 94-00334. Partial support for J.R.L. under U.S. Department of Energy, Office of Basic Energy Sciences, Grant no. DE-FG02-90ER45307 is gratefully acknowledged. We thank Anthony J. Garratt-Reed for experimental assistance with STEM.

REFERENCES

1. For a review of results up to about 1994, see A. P. Sutton and R. W. Balluffi, Interfaces in Crystalline

Materials, Oxford University Press, New York (1995).

- 2. E. I. Rabkin, W. Gust, W. Lojkowski and V. Paidar, Interface Sci. 1, 201 (1993).
- J. R. Lee, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass. (1995) [available through University Microfilms, Ann Arbor, Michigan].
- W. D. Kingery, J. B. Vander Sande and T. Mitamura, J. Am. Ceram. Soc. 62, 221 (1979).
- 5. F. Greuter and B. Blatter, Semicond. Sci. Technol. 5, 111 (1990).
- 6. F. Greuter, Solid State Ionics, 75, 67 (1995).
- 7. F. Stucki and F. Greuter, J. Appl. Phys. 57, 446 (1990).
- 8. J. R. Lee and Y.-M. Chiang, J.-R. Lee and Y.-M. Chiang, *Solid State Ionics*, **75**, 79 (1995).
- J.-R. Lee and Y.-M. Chiang, in *Materials Science* Forum (edited by A. C. Ferro, J. P. Conde and M. A. Fortes), Vol. 207–209, pp. 129–132, Transtec Publications, Zurich (1996).
- J. A. S. Ikeda, Y.-M. Chiang, A. J. Garratt-Reed and J. B. Vander Sande, J. Am. Ceram. Soc. 76, 2447 (1993).
- 11. M. Matsuoka, Jap. J. Appl. Phys. 10, 736 (1971).
- 12. J.-H. Hwang, T. O. Mason, and V. P. Dravid, J. Am. Ceram. Soc. 77, 1499 (1994).
- 13. D. McLean, *Grain Boundaries in Metals*, pp. 116–131, Clarendon Press, Oxford, (1957).
- G. Simmons and H. Wang, Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook. p. 326, MIT Press, Cambridge, MA (1971).
- 15. JCPDS Powder Diffraction File, International Centre for Diffraction Data, Swarthmore, Pennsylvania.
- J. W. Medernach and R. L. Snyder, J. Am. Ceram. Soc. 61, 494 (1978).
- G. M. Safronov, V. N. Batog, T. V. Stepanyuk and P. M. Fedorov, *Russ. J. Inorg. Chem.* 16, 460 (1971).
- Y.-M. Chiang, W. D. Kingery and L. M. Levinson, J. Appl. Phys. 53, 1765 (1982).
- H. L. Tuller and K.-K. Baek, in *Ceramic Transactions*, Vol. 41 (edited by L. M. Levinson and S.-I. Hirano), pp.19-34, The American Ceramic Society, Westerville, Ohio (1994).