Oxygen Diffusion in Bi$_2$O$_3$-doped ZnO

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In order to clarify the influence of Bi-doping on oxygen diffusion in ZnO, the bulk and grain boundary oxygen diffusion coefficients were measured in Bi$_2$O$_3$-doped ZnO polycrystals by means of the gas-solid exchange method using the isotope ^{18}O as the oxygen tracer. The experiments were performed on ZnO sintered samples containing 0.1, 0.3 and 0.5 mol% Bi$_2$O$_3$. The diffusion annealings were performed at 942, 1000 and 1092 °C, in an Ar+^{18}O$_2$ atmosphere under an oxygen partial pressure of 0.2 atm. After the diffusion annealings, the ^{18}O diffusion profiles were established by secondary ion mass spectrometry (SIMS). The results show an increase in the oxygen diffusion in the Bi$_2$O$_3$-doped ZnO, when compared to the oxygen diffusion in the undoped ZnO polycrystal under the same experimental conditions, both in bulk and in grain-boundaries. Moreover, it was observed that the higher the Bi$_2$O$_3$ concentration, the higher the oxygen diffusion. These results suggest that the incorporation of Bi$_2$O$_3$ increases the interstitial oxygen concentration which agrees with an interstitial diffusion mechanism both in bulk and in grain-boundaries.

Keywords: *oxygen diffusion, Bi$_2$O$_3$-doped ZnO, bulk diffusion, grain boundary diffusion*

1. Introduction

Knowledge of the defect structure and oxygen self-diffusion in ZnO is important for understanding and modeling of nonlinear current-voltage characteristics of ZnO-based varistors, as well as their degradation in service[1]. A number of studies with respect to oxygen diffusion in ZnO have been performed in the last few decades, but the oxygen diffusion mechanism is still not completely established. These previous studies have been compiled in reference 2. The most recent studies[2-5] suggest an interstitial mechanism for the oxygen diffusion in ZnO. According to Haneda et al.[3] and Sabioni et al.[4], the oxygen diffusion in ZnO takes place by means of doubly negatively charged interstitial oxygen. Moreover, Sabioni[5] also suggests the possibility of an interstitial mechanism with the interstitial oxygen having a null or single negative effective charge. The diffusion of null or negatively charged interstitial oxygen, suggested by Sabioni,[5] has been supported by theoretical calculations of migration mechanisms and diffusion of oxygen in zinc oxide performed by Erhart and Albe[2].

It is known that the electrical behavior of ZnO-based varistors is influenced by the incorporation of oxygen in this material, particularly, by diffusion along the grain-boundaries. As the defect chemistry and diffusion data used to describe the behaviour of ZnO-based varistors have been measured in undoped ZnO, it is necessary to obtain such data in ZnO containing impurities used in commercial varistors. The nonlinear current-voltage (I-V) characteristics of ZnO-based varistors are only achieved by doping the ZnO with large-sized ions like Bi and Pr.[1] Besides the segregants, other doping elements (e.g. Mn, Co, Ni) are used to enhance such nonlinearity. In addition, an oxidizing annealing also plays an important role on the nonlinearity by supplying oxygen excess that modifies the grain boundary chemistry[1].

This paper deals with the measurement of the oxygen diffusion in Bi$_2$O$_3$-doped ZnO. The bismuth oxide is the most important oxide incorporated in the ZnO to give it a nonlinear I-V behaviour. The purpose of the present study is to check the possible effect of Bi on the oxygen diffusion in ZnO. Based on previous considerations, and taking into account the valence of bismuth, it is expected that the bismuth incorporated in the ZnO should increase the oxygen diffusion by means of an interstitial mechanism. This is the first time that oxygen diffusion is measured in Bi$_2$O$_3$-doped ZnO ceramics obtained by sintering of mixed powders such as the commercial varistors. The experiments were performed on sintered samples containing 0.5 mol% Bi$_2$O$_3$ as in commercial varistors[6]. In order to check the effect of the Bi$_2$O$_3$ content, samples with 0.1 and 0.3% Bi$_2$O$_3$ were also prepared. The oxygen diffusion experiments were performed using the ^{18}O isotope as the oxygen tracer and the depth profiling was established by secondary ion mass spectrometry (SIMS). The results obtained for the bulk and the grain boundary diffusion coefficients are discussed and compared to available data for oxygen diffusion in undoped ZnO in similar experimental conditions.

2. Experimental Procedure

2.1. Material

The Bi_2O_3-doped ZnO samples were fabricated by the mechanical mixture of high-purity Bi_2O_3 and ZnO powders supplied by Alfa Aesar. The powder was cold pressed under a pressure of 600 MPa, and sintered at 1393 °C for 2 hours in an oxygen gas atmosphere. ZnO-Bi_2O_3 samples were prepared with three different Bi_2O_3 contents: 0.1, 0.3 and 0.5 mol %. The densities of the samples were superior to 97% of the theoretical density. The average grain-size ranged from 40 to 50 μm depending on the Bi_2O_3 concentration. For all compositions, there was strong pull out of the grains during the polishing. This was observed in all Bi_2O_3-ZnO samples, and the higher the Bi_2O_3 content, the higher the pull out of the grains. This problem of surface preparation was overcome by the versatility of the depth profiling technique used, which permits the analysis of very small regions on the surface.

2.2. Diffusion experiments

The samples were cut with the dimensions 4 x 4 x 2 mm, polished with diamond suspensions in a semi-automatic polishing machine and submitted to a pre-annealing in order to equilibrate the samples with the temperature and atmosphere to be used in the diffusion annealings. The oxygen diffusion experiments were performed by means of the gas-solid isotopic exchange method, using the isotope ^{18}O as the oxygen tracer. An Argon/$^{18}O_2$ atmosphere with oxygen partial pressure of 0.2 atm was used. The diffusion annealings were performed at 942, 1000 and 1092 °C.

2.3. Oxygen depth profiling by secondary ion mass spectrometry

The oxygen diffusion profiles were determined by secondary ion mass spectrometry (SIMS) using a CAMECA apparatus at "Groupe d´Étude de la Matière Condensée" - GEMAC/CNRS/Meudon-Bellevue, France. The SIMS analyses of the oxygen isotopes were established using a 10 keV Cs^+ primary ion source. During the SIMS analyses, the scanned area was 200 x 200 μm and the ionic signals were collected from a zone of 62 μm in diameter. The oxygen diffusion profiles of the ^{18}O isotope were determined from the signals of the negative secondary ions $^{16}O^-$ and $^{18}O^-$ by means of the relationship:

$$C(t) = \frac{I(^{18}O^-)}{I(^{16}O^-) + I(^{18}O^-)} \tag{1}$$

where C (t) is the ^{18}O concentration as a function of the sputtering time (t). Figure 1 shows the SIMS spectra for oxygen diffusion in ZnO-0.5 (mol %) Bi_2O_3, at 1000 °C. The depth of the craters was measured by means of a profilometer Tencor. The average sputtering rate was equal to the ratio: (depth of the crater)/(total sputtering time), and was assumed to be constant. For the SIMS analysis conditions used in this study, the sputtering rate was found to be ca. 0.22 nm/s. The ^{18}O penetration profiles, C (x) = f (depth), were then established from C (t) = f (t) by multiplying the sputtering time by the sputtering rate.

2.4. Determination of the oxygen bulk diffusion coefficient

The bulk diffusion coefficients were determined using a solution of Fick's second law for diffusion in a semi-infinite medium from a constant surface concentration given by[7]:

$$\frac{C(x) - C_s}{C_o - C_s} = erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{2}$$

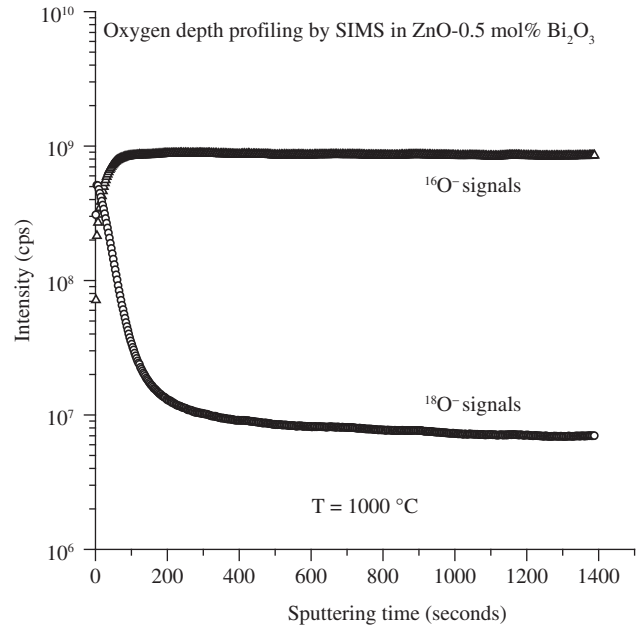**Figure 1.** SIMS analysis showing the $^{16}O^-$ and $^{18}O^-$ signals after oxygen diffusion in ZnO-0.5 mol % Bi_2O_3 at 1000 °C.

where C_s is the constant surface concentration of the tracer at the surface, C (x) is the tracer concentration at the depth x, C_o is the natural abundance of ^{18}O in ZnO (i.e. 0.2% of ^{18}O), D is the bulk diffusion coefficient, t is the annealing time and erf is the error function.

2.5. Determination of the oxygen grain boundary diffusion coefficient

In the experimental conditions used in this study, the diffusion regime is of B-type, which is defined by Harrison's conditions[8] given by:

$$\Phi > (Dt)^{1/2} > \delta/2 \tag{3}$$

where δ is the grain boundary width, D is the bulk diffusion coefficient and Φ is the grain-size.

For B-type intergranular diffusion, it is possible to determine the product D´δ, where D´ is the grain boundary diffusion coefficient, by means of Le Claire´s relationship[9]:

$$D'\delta = 0.661\left(\frac{4D}{t}\right)^{1/2}\left(-\frac{d\ln C(x)}{dx^{6/5}}\right)^{-5/3} \tag{4}$$

where D is the bulk diffusion coefficient and t is the diffusion time.

3. Results and Discussion

3.1. Oxygen diffusion coefficients in Bi_2O_3-doped ZnO

Figure 1 shows a typical SIMS spectra displaying the signals of the negative secondary ions $^{16}O^-$ and $^{18}O^-$ measured in ZnO-0.5 mol % Bi_2O_3 after a diffusion treatment at 1000 °C. The ^{18}O depth concentration profiles were deduced from the SIMS spectra using the procedure previously described.

A typical diffusion profile for the oxygen diffusion in ZnO-0.5 mol % Bi_2O_3 after diffusion at 1000 °C, for 8 hours 30 minutes in an Ar/$^{18}O_2$ atmosphere, is given in Figure 2. The diffusion profile clearly shows two different diffusion mechanisms. The first part of the diffusion profile, of high gradient dC/dx (C = [^{18}O]), corresponds to the bulk diffusion and the second part, of low gradient

dC/dx, i.e. the tail of the profile, is characteristic of the diffusion along the grain-boundaries in a B-type diffusion regime[7]. Similar profiles were obtained in all cases. From these diffusion profiles, two oxygen diffusion coefficients were determined: in bulk (D) and in grain boundary (in fact D´δ). The bulk diffusion coefficient was determined by fitting Equation 2 to the first part of the diffusion profile by non-linear regression. The product D´δ was determined by means of Equation 4 where the gradient dln/dx$^{6/5}$ was calculated from the tail of the diffusion profile in the plot of ln C (x) versus x$^{6/5}$ as shown in Figure 3. The experimental conditions and the results obtained for bulk and grain boundary diffusion coefficients in Bi$_2$O$_3$-doped ZnO are listed in Table 1. According to the data in Table 1, the ratio D´δ/D is approximately 10^{-2}. Taking into account the usual value of δ for ceramics of 1 nm, determined by Atkinson and Taylor[10], the oxygen grain boundary diffusion coefficient can be estimated to be five orders of magnitude greater than the bulk diffusion coefficient.

3.2. Comparison of the oxygen diffusivities in undoped ZnO and in Bi$_2$O$_3$-doped ZnO

In order to compare the oxygen diffusivity in Bi$_2$O$_3$-doped ZnO with the oxygen diffusivity in undoped ZnO, data of oxygen diffusion measured in polycrystalline ZnO in similar experimental conditions to those of the present study were taken into account. The only data available for oxygen diffusion in polycrystalline ZnO, in similar conditions to those used in the present study is given in reference 1. The oxygen bulk and grain boundary diffusion coefficients were measured under an oxygen pressure of 0.2 atm, between 900 and 1100 °C. The Arrhenius equations describing the dependence on temperature of the oxygen bulk and grain boundary diffusions in polycrystalline ZnO are given by the relationships[1]: D (cm^2/s) = 1.42 x 10^{-5} exp [–274 (kJ/mol)/ RT] for bulk diffusion and D'δ (cm^3/s) = 1.62 x 10^{-7} exp [–280 (kJ/mol)/ RT] for the grain boundary diffusion. As for the Bi$_2$O^3-doped ZnO, the grain boundary is a fast path for oxygen diffusion in ZnO. In fact, the ratio D´δ/D is also ca. 10^{-2}, and assuming the typical value of 1 nm for δ, it is found that the oxygen grain boundary diffusion coefficient in ZnO is five orders of magnitude greater than the bulk diffusion coefficient. This shows that the grain boundary is a fast path for oxygen diffusion both in ZnO and in Bi$_2$O$_3$-doped ZnO.

The Arrhenius graph in Figure 4 allows a comparison of the oxygen bulk and grain boundary diffusion coefficients in undoped ZnO and in ZnO-0.5 mol % Bi$_2$O$_3$. The oxygen bulk diffusion coefficient in ZnO-0.5 mol % Bi$_2$O$_3$ is greater than in ZnO. The oxygen grain boundary diffusion coefficient in ZnO-0.5 mol % Bi$_2$O$_3$ is also greater than in ZnO. This indicates that the incorporation of Bi$_2$O$_3$ in ZnO increases the oxygen diffusivity both in the bulk and in the grain-boundaries.

3.3. Effect of Bi$_2$O$_3$ content on oxygen diffusion in Bi$_2$O$_3$-doped ZnO

In order to check the effect of the Bi$_2$O$_3$ content on the oxygen diffusivity in Bi$_2$O$_3$-doped ZnO, the oxygen diffusion was also
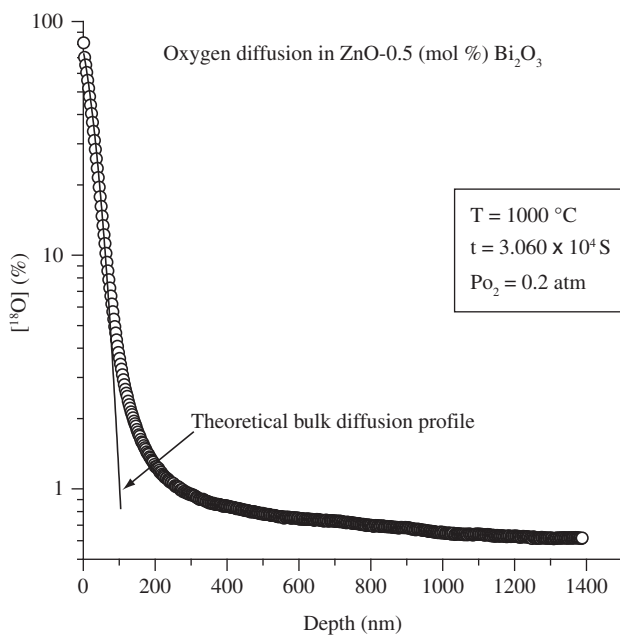

Figure 2. Oxygen diffusion profile in ZnO-0.5 mol % Bi$_2$O$_3$ after diffusion at 1000 °C.
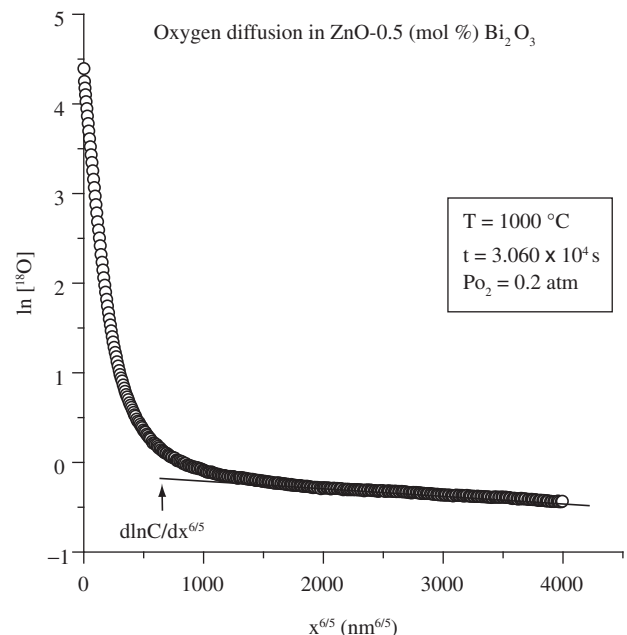

Figure 3. Oxygen concentration plot against x$^{6/5}$ for oxygen diffusion in ZnO-0.5 mol % Bi$_2$O$_3$ at 1000 °C (same experiment than in Figure 2). The slope of the straight line corresponds to the gradient dlnC/dx$^{6/5}$.

Table 1. Oxygen diffusion in Bi$_2$O$_3$-doped ZnO. PO$_2$ = 0.2 atm.

T (°C)	Bi$_2$O$_3$ (mol %)	t (s)	D (cm^2/s)	δ D´ (cm^3/s)
942	0.5	8.304 x 10^4	8.6 x 10^{-17}	8.7 x 10^{-19}
1000	0.1	3.060 x 10^4	1.1 x 10^{-16}	3.0 x 10^{-18}
1000	0.3	3.060 x 10^4	1.8 x 10^{-16}	3.4 x 10^{-18}
1000	0.5	3.060 x 10^4	2.7 x 10^{-16}	8.1 x 10^{-18}
1092	0.5	1.080 x 10^4	3.2 x 10^{-15}	2.4 x 10^{-17}

Figure 4. Arrhenius plot for oxygen diffusion in undoped ZnO and in ZnO-0.5 mol % Bi_2O_3.

Figure 5. Effect of the Bi_2O_3 content on the oxygen diffusion in Bi_2O_3-doped ZnO.

measured in ZnO containing 0.1 or 0.3 (mol %) of Bi_2O_3, at 1000 °C, in the same $Ar/^{18}O_2$ atmosphere (oxygen partial pressure of 0.2 atm). Figure 5 shows the dependence of the oxygen diffusivity in ZnO on the Bi_2O_3 content. For comparison, the data of reference 1 for undoped ZnO (0 mol % Bi_2O_3), obtained in the same experimental conditions, were used. The oxygen diffusion, both in bulk and in grain boundary, slightly increases with the Bi_2O_3 content. As mentioned above, the most recent studies[2-5] on oxygen diffusion in ZnO have suggested an interstitial mechanism for oxygen diffusion in ZnO. The incorporation of Bi_2O_3 into ZnO should increase the oxygen interstitial concentration and, consequently, the oxygen diffusion by an interstitial mechanism. This may be shown assuming, for example, that oxygen diffusion takes place in ZnO by means of doubly negatively charged interstitial oxygen (O´i). The incorporation of Bi_2O_3 in ZnO may be described by the following relationship:

$$Bi_2O_3 \xrightarrow{ZnO} 2Bi_{Zn}^{\circ} + 2O_o^x + O_i^{''} \tag{5}$$

Equation 5 suggests that the incorporation of Bi introduces interstitial oxygen in the structure. It is known that the diffusion coefficient is proportional to the concentration of the point defect responsible for the diffusion. Therefore, for an interstitial diffusion mechanism, the oxygen diffusion coefficient should be proportional to the interstitial oxygen concentration, i.e. [D] α [O´i] and, consequently, the higher the interstitial oxygen concentration, the higher is the oxygen diffusion coefficient. This conclusion does not depend on the interstitial oxygen charge and agrees with the results observed in the present study. It is important to note that the same effect is observed in bulk and grain boundaries, which implies that the diffusion mechanism by means of interstitial oxygen is the same in bulk and in grain-boundaries.

It is not the purpose of the present paper to discuss the relation between the oxygen diffusion in Bi_2O_3-doped ZnO and the electrical behavior of ZnO-based varistors, but only to supply new information for discussion in further specific studies on varistor modeling. In fact, the ZnO-based commercial varistors have other additives as Sb_2O_3,
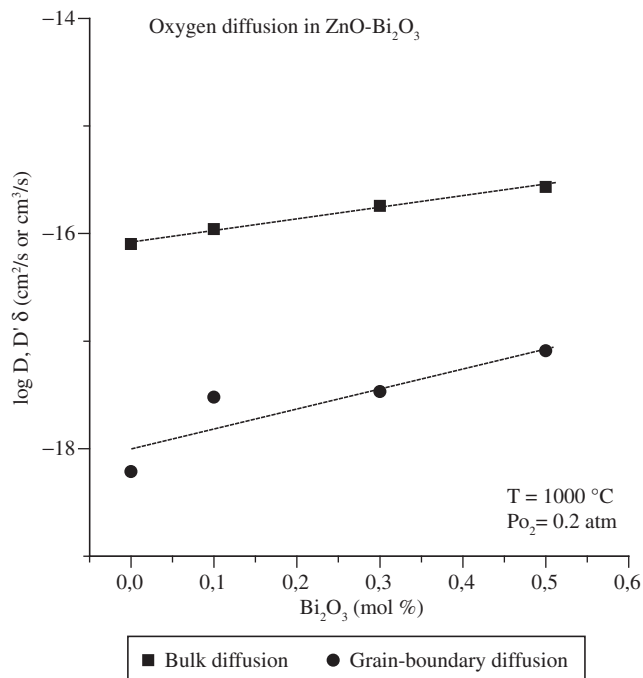
CoO, MnO_2, Cr_2O_3, NiO, etc. Measurements of oxygen diffusion coefficients in a commercial varistor are in progress and will be the subject of a future paper.

4. Conclusion

For the first time oxygen diffusion coefficients were measured in Bi_2O_3-doped ZnO ceramics obtained by sintering of mixed powders such as the commercial varistors. The results show an increase in the oxygen diffusion in Bi_2O_3-doped ZnO, both in bulk and in grain-boundaries, when compared to the oxygen diffusion in undoped ZnO polycrystal under the same experimental conditions. Moreover, it was observed that the higher the Bi_2O_3 concentration, the higher the oxygen diffusion. These results suggest that the incorporation of Bi_2O_3 increases the interstitial oxygen concentration which agrees with an interstitial diffusion mechanism both in bulk and in grain-boundaries. The results also show that the grain boundary is a fast path for the oxygen diffusion in Bi_2O_3-doped ZnO such as previously observed in undoped ZnO.

Acknowledgments

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