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Diffusion of the ^{65}Zn Radiotracer in ZnO Polycrystalline Ceramics

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Zinc self-diffusion coefficients were measured in polycrystalline ZnO of high density (>99% of the theoretical density) and of high purity (> 99.999%). The diffusion experiments were performed from 1006 to 1377 °C, in oxygen atmosphere, for times between 16 and 574 h. The diffusion profiles were established by means of Residual Activity Method using the ^{65}Zn radioactive isotope as zinc tracer. In our experimental conditions, the zinc volume diffusion coefficients can be described by the following Arrhenius relationship: $D(cm^2/s) = 1.57\times10^{-3} \exp[(-2.66 \pm 0.26)\ eV/kT]$. In the same experimental conditions, the grain-boundary diffusion coefficients are approximately 4 orders of magnitude greater than the volume diffusion coefficients, and can be described by the Arrhenius relation: $D'\delta\ (cm^3/s) = 1.59\times10^{-6} \exp[(-2.44 \pm 0.45)\ eV/kT]$, where D' is the grain-boundary diffusion coefficient and δ is the grain boundary width.

Keywords: *zinc oxide, zinc diffusion, grain-boundary, varistor*

1. Introduction

The transport properties and the defect chemistry of zinc oxide have been intensivelly studied in the last decades due to, principally, the utilization of this material in ZnO-based varistors.

The non-linear current-voltage characteristics of ZnO varistors, as well as its degradation in operation (loss of its varistor property) are grain-boundary phenomena involving interaction between point defects and ionic diffusion[1,2]. The understanding and the modelling of these phenomena demand the knowledge of the defect structure and of the diffusional processes in ZnO.

In spite of numerous previous studies about diffusion and defect in ZnO, there is still lack of reliable defect and diffusion data as shown by Tomlins *et al.*[3,4].

The present work is part of a wide project concerned with the study of diffusion and defects in ZnO[5], and deals with the study of the zinc diffusion in ZnO.

While previous works[4,6,7] about zinc diffusion in ZnO were performed in single crystalline samples, this work is dedicated to the determination of zinc diffusion in polycrystals, like ZnO varistors, in order to determine the zinc volume and grain-boundary diffusion coefficients.

In previous works, performed by Kim[6], and by Moore and Williams[7], it was used the ^{65}Zn radioactive isotope as zinc tracer and the diffusion profiles were obtained by a serial sectioning technique and by counting the activity in each removed section.

Recently, Tomlins *et al.*[4] have used the ^{70}Zn stable isotope as tracer and analysed the diffusion profiles by secondary ion mass spectrometry (SIMS). In the present work, the methodology used is different of the previous works, and consisted in using the ^{65}Zn radioactive isotope as tracer, but with depth profiling by means of the residual activity method or Gruzin's method[8].

2 Experimental Procedure

2.1 Material

The polycrystalline ZnO samples were fabricated by using high-purity powder obtained from Alfa Aesar. The

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impurity content was less than 10 ppm (elements detected: 0.1 ppm Fe and 1 ppm Pb). The powder was cold pressed and sintered at 1400 °C, for 4 h in oxygen atmosphere. No additive was used as powder agglomerant in the sintering experiments.

The sintered ZnO had high density (> 99% of the value of the theoretical density) and grain size of 20 μm. These samples were resintered for 72 h at 1393 °C, in oxygen atmosphere, in order to increase the grain size above 80 μm.

A typical microstructure of the ZnO samples used in this work, after thermal etching at 1150 °C, for 1 h, in air, is shown in Fig. 1.

For the diffusion experiments, samples of dimensions 17 mm × 17 mm × 3 mm, were polished with diamond paste, and submitted to pre-annealing in order to equilibrate the samples with the temperature and atmosphere to be used in the diffusion annealings.

2.2 Preparation of the ^{65}Zn radioactive tracer

The zinc tracer used in this work was the radioactive isotope ^{65}Zn. This isotope has a half-life of 244.1 days and decays emitting the radiations γ (1.1154 and 0.820 MeV) and β^+ (0.324 MeV).

The ^{65}Zn radiotracer was prepared by irradiation of a $ZnCl_2$ solution (99.999%), under a neutron flux of 6.6×10^{11} neutrons/cm^2.s, for 4 h, in TRIGA reactor (250 kW) at CDTN/CNEN (Belo Horizonte /MG).

2.3 Deposition of the tracer

A drop of the irradiated $ZnCl_2$ was deposited on the polished surface of the sample, previously thermodinamically equilibrated. The drop was carefully spread on the surface, slowly dried, and then oxidized at 500 °C, for 2 h, in air.

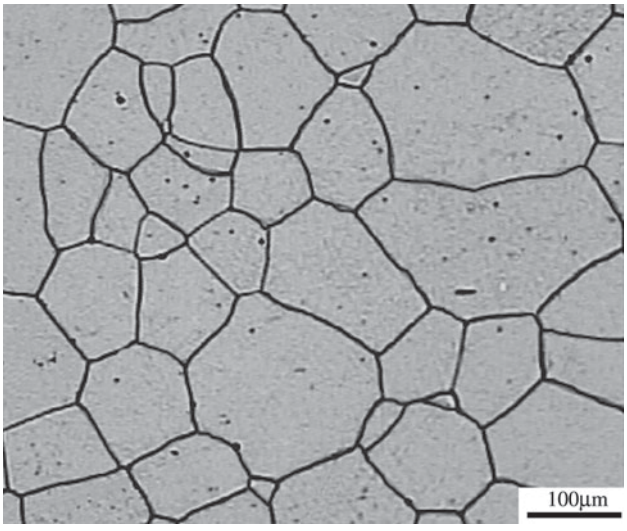

Figure 1. Typical microstructure of polycrystalline ZnO used in this work, after thermal etching at 1150 °C, for 1 h, in air.

2.4 Diffusion experiments

The diffusion experiments were performed from 1006 to 1377 °C, in oxygen atmosphere, for times between 16 and 574 h. These diffusion treatments were performed in a tubular furnace of super kanthal resistance.

In order to minimise the evaporation of the tracer and of the ZnO samples, which is significative above 1100 °C, the samples were placed in a ZnO crucible for the diffusion annealings.

2.5 Determination of the ^{65}Zn diffusion profiles

After the diffusion annealings, about 1 mm in thickness of material was removed from each lateral face and back. This operation was performed to remove ^{65}Zn tracer eventually diffused along the lateral surface, followed by diffusion into volume, where it would be counted.

The diffusion profiles of ^{65}Zn were determined by means of the Gruzin's Method or Residual Activity Method [8].

In this method, sections of the sample are removed, and the activity remaining in the sample after each sectioning is measured. The sectioning was performed by mechanical abrasion using a high precision grinder. The thickness of the removed section was determined by measuring the mass of the sample before and after the sectioning.

The counting of the γ-radiation (1.1154 MeV) was performed using a NaI(Tl) scintillation counter (EGεG ORTEC - Scintipack - Model 296). The duration of each counting was 45 min.

The diffusion profiles of ^{65}Zn were established by plotting the residual activity (I), after each sectioning, versus the depth (x) of the sectioning.

The residual activity method is applicable if the radiation used is absorbed exponentially, with a linear absorption coefficient μ. If I is the residual activity after the nth section, it can be show that [8]:

$$\mu I(x_n) - \frac{dI(x_n)}{dx_n} = kC(x_n) \qquad (1)$$

whatever the functional form of C(x). This equation can be simplified if the used radiation is only slightly absorbed, as in the case of the γ radiation used in this work. The simplified equation is given by:

$$\frac{dI(x_n)}{dx_n} = -kC(x_n) \qquad (2)$$

3. Results and Discussion

3.1 ^{65}Zn volume diffusion

Figure 2 shows a typical diffusion profile after diffusion of the ^{65}Zn at 1300 °C, in oxygen atmosphere, for 29 h. The diffusion profile shows two regions.

The first part of the profile, of high gradient dI/dx, corresponds to the volume diffusion and the second part of profile of low gradient dI/dx, ie, the tail of the profile, is a characteristic of the diffusion along the grain-boundaries [8].

In our experimental conditions, diffusion from an instantaneous source, Eq. (2) has the following form[8].

$$-\frac{dI(x_n)}{dx_n} = k\frac{Q}{\sqrt{\pi Dt}}\exp\left(-\frac{x_n^2}{4Dt}\right) \quad (3)$$

Resolving Eq. (3), it is obtained the following relationship for I as a function of x[9]:

$$\frac{I}{I_0} = \mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (4)$$

where the erfc function is given by

$$\mathrm{erfc}\, u = 1 - \frac{2}{\pi^{1/2}}\int_0^u \exp(-u^2)du$$

The fit of Eq.4 to the first region of the diffusion profile, as shown in Fig. 2, gives the value of the volume diffusion coefficient (D). Figure 3 shows the dependence on temperature of the diffusion coefficients determined in this work, which can be described by an Arrhenius equation given by:

$$D(cm^2/s) = 1.7 \times 10^{-3} \exp\left[\frac{(-2.66 \pm 0.26)eV}{kT}\right] \quad (5)$$

Figure 3 also shows the comparison of the results of the present work with those previously published[6-8]. Our results and those recently determined by Tomlins *et al.* show good agreement for the volume diffusion coefficients values.

Further experiments of zinc diffusion as function of the oxygen pressure have been performed in order to determine the zinc diffusion mechanism (vacancy or insterstitial mechanism) in ZnO, and will be the subject of another paper.

3.2 ^{65}Zn grain-boundary diffusion

According to Harrison's conditions[10], our ^{65}Zn intergranular diffusion experiments are of B-type:

$$\delta << (Dt)^{1/2} < \Phi/2 \quad (6)$$

where δ is the grain-boundary width, D is the volume 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. For the experimental conditions used in this work, the product D'δ is calculated by using the Suzuoka's model[11] through the relationship:

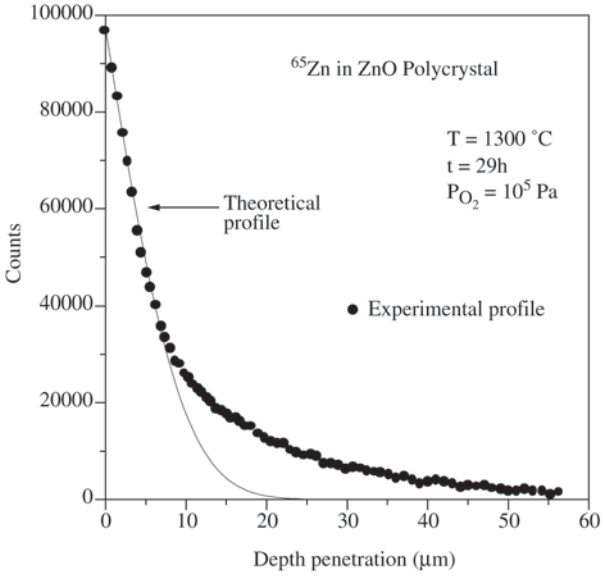

Figure 2. Diffusion profile for the isotope ^{65}Zn in ZnO polycrystal at 1300 °C.

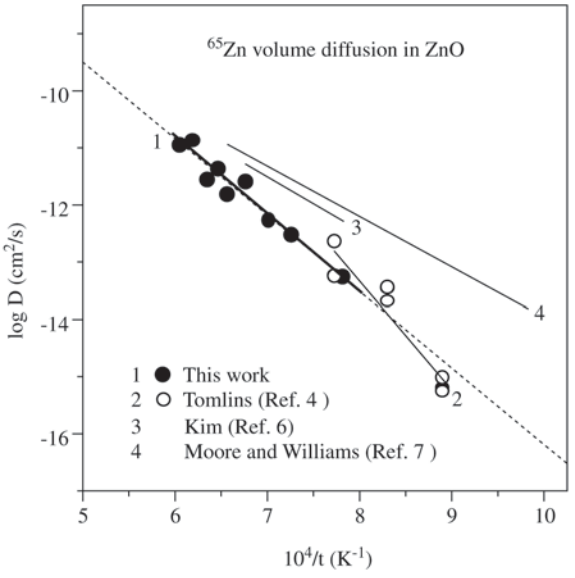

Figure 3. Comparison of volume diffusion coefficients obtained in this work with those available in the literature.

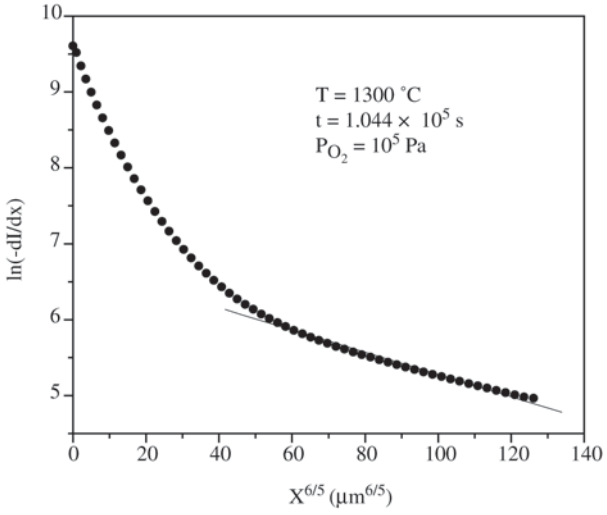

Figure 4. Plot of ln(-dI/dx) *vs.* $x^{6/5}$, after diffusion at 1300 °C.

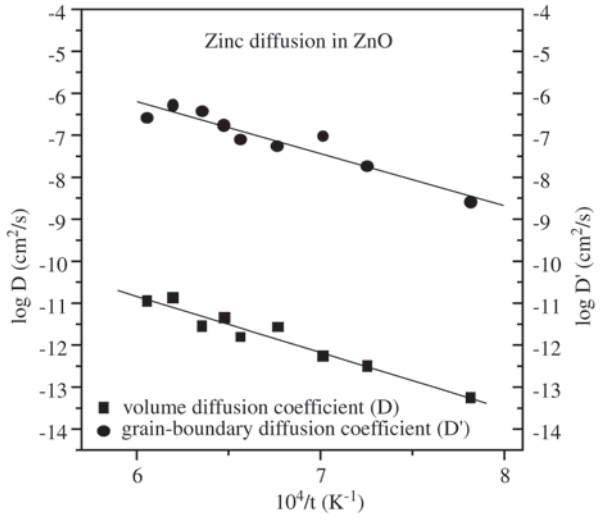

Figure 5. Comparison of volume diffusion coefficients (D) and grain-boundary diffusion coefficients (D') obtained in the same experimental conditions.

Table 1. Experimental conditions and results for zinc diffusion in polycrystalline ZnO

T(°C)	t(s)	D'δ(cm³/s)	D(cm²/s)	D'/D
1006	2.0664×10^{6}	2.47×10^{-16}	5.34×10^{-14}	4.62×10^{4}
1105	7.9188×10^{5}	1.75×10^{-15}	2.98×10^{-13}	5.87×10^{4}
1151	3.3180×10^{5}	1.30×10^{-14}	5.10×10^{-13}	2.55×10^{5}
1203	1.0080×10^{5}	5.14×10^{-15}	2.57×10^{-12}	2.00×10^{4}
1249	1.7280×10^{5}	7.48×10^{-15}	1.52×10^{-12}	4.92×10^{4}
1271	1.1082×10^{5}	1.67×10^{-14}	4.21×10^{-12}	3.97×10^{4}
1300	1.0440×10^{5}	7.12×10^{-14}	2.69×10^{-12}	2.65×10^{5}
1341	6.4800×10^{4}	4.97×10^{-14}	1.31×10^{-11}	3.79×10^{4}
1377	5.7480×10^{4}	2.20×10^{-14}	1.09×10^{-11}	2.02×10^{4}

$$D'\delta = 2(D/t)^{1/2}\left(-\frac{\partial \ln(-dI/dx)}{\partial x^{6/5}}\right)^{-5/3}(0.72\beta^{0.008})^{5/3} \quad (7)$$

where the parameter β is given by:

$$\beta = \left[(0.70)^{-1}\left(-\frac{\partial \ln(-dI/dx)}{\partial x^{6/5}}\right)(Dt)^{3/5}\right]^{-1/0.582} \quad (8)$$

The gradient $\left(-\frac{\partial \ln(-dI/dx)}{\partial x^{6/5}}\right)$ is calculated from the tail of the diffusion profile in a plot of ln(-dI/dx) versus $x^{6/5}$ as shown in Fig. 4.

The experimental conditions used and the results obtained for the grain-boundary diffusion are listed in Table 1.

The dependence on temperature for the product D'δ can be described by the following Arrhenius equation:

$$D'\delta\ (cm^3/s) = 1.59\times10^{-6}\exp[(-2.44 \pm 0.45)eV/kT] \quad (9)$$

Equation 9 can be rewriten on the following form:

$$D'(cm^2/s) = (1/\delta)1.59\times10^{-6}\exp[(-2.44 \pm 0.45)eV/kT] \quad (10)$$

Assuming for δ the usual value[12] of 1 nm, the ^{65}Zn grain-boundary diffusion coefficient can be estimated from Eq. 10.

Figure 5 shows the comparison between the volume diffusion coefficients (D) and the grain-boundary diffusion coefficients (D'). It is clear from Table 1 that the ratio D'/D is greater than 10^4. This shows that the grain-boundary is a fast path for zinc diffusion in ZnO. There is no data in literature about zinc grain-boundary diffusion coefficients in ZnO for comparison with our results.

4. Conclusions

1. Zinc volume diffusion coefficients and zinc grain-boundary diffusion coefficients in ZnO were measured by means of the residual activity method using the ^{65}Zn as zinc tracer. The diffusion coefficients were studied as a function of the temperature under an oxygen pressure of 10^5 Pa. The product D'δ for the

intergranular diffusion was determined using the Suzuoka model for B-type diffusion.

2. For the first time an Arrhenius' equation was established for zinc grain-boundary diffusion in ZnO.
3. The activation energy for zinc volume diffusion is about 2.66 eV, and the activation energy for intergranular diffusion is 2.44 eV.
4. The zinc grain-boundary diffusion coefficients are ca. 4 orders of magnitude greater than the volume diffusion coefficients, in the same experimental conditions, which means that the grain-boundary provides a fast path for zinc diffusion in ZnO.

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