Short communication

About the oxygen diffusion mechanism in ZnO

Antônio Claret Soares Sabioni

Laboratório de Difusão em Materiais, Departamento de Física, Universidade Federal de Ouro Preto, Ouro Preto 35400-000, Brazil

Abstract

The more recent works dealing with the study of oxygen self-diffusion in ZnO have shown that the oxygen diffusion takes place by means of doubly negatively ionized interstitial oxygen. This oxygen diffusion mechanism in zinc oxide is reviewed and based on experimental data of oxygen self-diffusion and electrical conductivity; for Al-doped and undoped ZnO, it is suggested that oxygen self-diffusion in ZnO takes place by means of an interstitial mechanism, but with the interstitial oxygen having a null or a single negative effective charge.
© 2003 Elsevier B.V. All rights reserved.

Keywords: ZnO; Al-doped ZnO; Oxygen self-diffusion; Diffusion mechanism

The oxygen self-diffusion in ZnO has been intensively studied in the last few decades. These previous works have been reviewed in Refs. [1,2]. The knowledge of self-diffusion in ZnO is important for understanding and modelling of the nonlinear current–voltage characteristics of ZnO-based varistors, as well as of their degradation (loss of the varistor property) in service [3–5].

In spite of these previous works, the oxygen diffusion mechanism in ZnO is not completely established yet. However, the two more recent publications about oxygen diffusion in ZnO, that of Haneda et al. [2] and of Sabioni et al. [6], have shown good agreement in relation to the oxygen diffusion mechanism in ZnO. According to these authors, the oxygen self-diffusion in ZnO takes place by means of an interstitial mechanism, through doubly negatively ionized interstitial oxygen, which is supported by results of diffusion experiments in both works.

The aim of this study is to review the value of the effective charge of the interstitial oxygen, and to check if the interstitial oxygen is really doubly negatively ionized, as it has been proposed in Refs. [2,6]. To discuss the charge state, experimental data about oxygen diffusion in pure and Al-doped ZnO [2,6], and also experimental data on electrical conductivity of pure and Al-doped ZnO, will be taken into account. The data about electrical conductivity used in this work are described elsewhere [7,8].

The formation of interstitial oxygen on oxygen sublattice of the pure ZnO, as an intrinsic defect, results from the anti-Frenkel disorder. Using Kröger and Vink notation [9], the anti-Frenkel disorder in ZnO can be described by the following general equation:

$$O_O^x = O_i^{\alpha'} + V_O^{\alpha\circ} \tag{1}$$

where O_O^x is an oxygen ion in its regular site, $O_i^{\alpha'}$ (O_i^x, O_i' or O_i'') is an oxygen interstitial and $V_O^{\alpha\circ}$ (V_O^x, V_O° or $V_O^{\circ\circ}$) is an oxygen vacancy. The superscript denotes the effective charge of the defect, or ion, relative to the perfect crystal lattice. A dot (°) represents a positive effective charge, a prime (′) indicates a negative effective charge, x corresponds to a null effective charge, and α is the ionization degree (number of positive or negative effective charges). It means that there are three possible charge states for the interstitial oxygen and for the oxygen vacancy.

It is known that the diffusion coefficient (D) is proportional to the concentration of the point defects responsible for the diffusion [10]. Assuming that oxygen diffusion takes place in ZnO by means of doubly negatively charged interstitial oxygen (O_i''), the oxygen diffusion coefficient should be proportional to the interstitial oxygen concentration, i.e., $D \propto [O_i'']$. Therefore, the higher the interstitial oxygen concentration, the higher is the oxygen diffusion coefficient.

E-mail address: sabioni@iceb.ufop.br (A.C. Soares Sabioni).

According to Haneda et al. [2], the oxygen diffusion in Al-doped ZnO is greater than in pure ZnO. This result was recently confirmed by Sabioni et al. [6]. The increasing of the oxygen diffusion coefficient in Al-doped ZnO compared to pure ZnO was explained by the following defect-formation-reaction equation:

$$Al_2O_3 \xrightarrow{ZnO} 2Al_{Zn}^{\circ} + 2O_O^x + O_i'' \qquad (2)$$

Eq. (2) shows that the oxygen diffusion in Al-doped ZnO is enhanced due to the increasing of the concentration of doubly negatively charged interstitial oxygen.

In the previous works [2,6], a vacancy mechanism for oxygen diffusion was discarded, because, in such a case, the Al incorporation should decrease the oxygen vacancy concentration, and consequently the oxygen diffusivity, as follows:

$$Al_2O_3 + V_O^{\cdot\cdot} \xrightarrow{ZnO} 2Al_{Zn}^{\circ} + 3O_O^x \qquad (3)$$
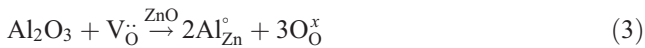
So, a model for oxygen diffusion in ZnO by means of a vacancy mechanism has no experimental support [2,6].

Undoped ZnO is an n-type semiconductor [7,8], and its electrical conductivity can be described by

$$\sigma = ne\mu \qquad (4)$$

where n is the concentration of electrons, e is the electronic charge and μ is the mobility.
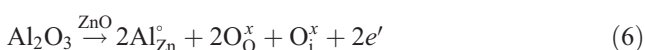
According to Refs. [7,8], the electrical conductivity of Al-doped ZnO is greater than that of pure ZnO. As pure ZnO is an n-type semiconductor, this enhancement of the electrical conductivity in Al-doped ZnO is due to the increasing of the concentration of electrons, and has been described by the following model [7,8]:

$$Al_2O_3 \xrightarrow{ZnO} 2Al_{Zn}^{\circ} + 2O_O^x + \frac{1}{2}O_2(g) + 2e' \qquad (5)$$
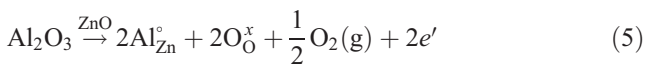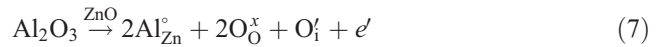
Eq. (5) shows that the incorporation of Al in ZnO increases the concentration of electron and consequently the electrical conductivity of the ZnO. This equation explains the increase of the electrical conductivity, but not the enhancement of the oxygen diffusion in Al-doped ZnO by means of an interstitial mechanism.

On the other hand, Eq. (2) explains the increasing of oxygen diffusion by means of an interstitial mechanism, but not the increasing of the electrical conductivity in Al-doped ZnO.

To conciliate the experimental results for oxygen diffusion with those for electrical conductivity, the following alternate models are proposed:

$$Al_2O_3 \xrightarrow{ZnO} 2Al_{Zn}^{\circ} + 2O_O^x + O_i^x + 2e' \qquad (6)$$

replacing O_i'' by $O_i^x + 2e'$, in Eq. (2), or

$$Al_2O_3 \xrightarrow{ZnO} 2Al_{Zn}^{\circ} + 2O_O^x + O_i' + e' \qquad (7)$$

replacing O_i'' by $O_i' + e'$, in Eq. (2).

Eq. (6) or (7) justifies either the increase of the electrical conductivity or the oxygen diffusion in Al-doped ZnO. These equations lead to a new and interesting aspect concerning the oxygen diffusion in ZnO, i.e., oxygen diffusion in ZnO takes place by means of an interstitial mechanism, with the interstitial oxygen having a single negative charge (O_i') or a null effective charge (O_i^x). This observation is important because the role of interstitial oxygen, until recently, i.e., before the works in Refs. [2,6] were published, had been neglected in oxygen diffusion studies [1].

To establish the correct value of the effective charge, measurements of oxygen diffusion coefficients, as a function of the oxygen pressure, must be performed in undoped ZnO.

The extrinsic defect concentration in a nonstoichiometric oxide, like ZnO, as a function of the temperature and oxygen pressure, can be described by [10]:

$$[d] = A(p_{O_2})^n \exp\left(-\frac{\Delta\tilde{G}_d^f}{kT}\right)$$

where d generically represents an electronic or atomic point defect, e.g., $d \equiv O_i^{\alpha'}$ is the interstitial oxygen, A is a constant, p_{O_2} is the oxygen partial pressure, n is a dimensionless parameter that depends on the nature and charge of the point defect, $\Delta\tilde{G}_d^f$ is the apparent formation energy of the defect and k is the Boltzmann constant.

As the diffusion coefficient is proportional to the point defect concentration, i.e., $D \propto [d]$, therefore, at a given temperature, $D \propto (p_{O_2})^n$, and in a plot of log D versus log p_{O_2}, it is possible to determine n through the following relationship:

$$n = d\log D / d\log p_{O_2}$$

For an interstitial oxygen, there are many possible values for n. To establish these n values, it will be assumed that: (i) ZnO is a metal excess oxide [4]; (ii) ZnO is an n-type semiconductor [7,8]; and (iii) zinc volume diffusion [11] is greater than oxygen volume diffusion [6] in pure ZnO.

To satisfy conditions (i) and (ii), the majority atomic defect in pure ZnO should be $Zn_i^{\beta\circ}$ ($\beta = 1$ or 2) or $V_O^{\delta\circ}$ ($\delta = 1$ or 2), electrically equilibrated by e'. However, the oxygen vacancy ($V_O^{\delta\circ}$) will not be assumed to be a possible majority atomic defect due to the condition (iii), and, in addition, recent works [2,6] have shown no experimental evidence for the role of this defect in oxygen diffusion.

As the ZnO defect structure is not well established yet, the formation of minority and majority defects in this material will be described by general equations as follows:

$$ZnO = Zn_i^{\beta\circ} + \beta e' + \frac{1}{2}O_2(g) \tag{8}$$

$$\frac{1}{2}O_2(g) = O_O^x + V_{Zn}^{\gamma'} + \gamma h^\circ \tag{9}$$

$$O_O^x = V_O^{\delta\circ} + \delta e' + \frac{1}{2}O_2(g) \tag{10}$$

$$\frac{1}{2}O_2(g) = O_i^{\eta'} + \eta h^\circ \tag{11}$$

The equilibrium constants of reactions (8)–(11) are obtained by applying the mass action law, and can be expressed by the following equations:

$$K^f_{(Zn_i^{\beta\circ})} = [Zn_i^{\beta\circ}][e']^\beta p_{O_2}^{1/2} \tag{12}$$

$$K^f_{(V_{Zn}^{\gamma'})} = [V_{Zn}^{\gamma'}][h^\circ]^\gamma p_{O_2}^{-1/2} \tag{13}$$

$$K^f_{(V_O^{\delta'})} = [V_O^{\delta\circ}][e']^\delta p_{O_2}^{1/2} \tag{14}$$

$$K^f_{O_i^{\eta'}} = [O_i^{\eta'}][h^\circ]^\eta p_{O_2}^{-1/2} \tag{15}$$

In this analysis of defects in ZnO, it is also necessary to consider the intrinsic equilibrium between electronic carriers: $null = e' + h^\circ$, with the electroneutrality condition given by $K_G = [e'][h^\circ]$.

Taking into account conditions (i), (ii) and (iii) above, the electrical neutrality condition in pure ZnO should be $\beta[Zn_i^{\beta\circ}] = [e']$ ($\beta = 1$ or 2). Table 1 shows the n values for the oxygen partial pressure dependence of the possible majority and minority defects in pure ZnO using that electrical neutrality condition.

In Al-doped ZnO, the observed electrical behaviour is of an n-type extrinsic semiconductor. In this doped material, the electroneutrality condition should be given by:

$$[Al_{Zn}^\circ] = [e'] \tag{16}$$

Eq. (16) is another reason to describe the incorporation of Al in ZnO by means of Eq. (6) or (7), and not by Eq. (2). Table 1 also shows the dependence on oxygen partial pressure of the possible defects in Al-doped ZnO using the electrical neutrality condition given by Eq. (16).

Therefore, measurements of oxygen diffusion coefficients as a function of the oxygen pressure may lead to the identification of the correct ionization degree of the interstitial oxygen responsible for the oxygen diffusion in ZnO.

There are only two works in the literature dealing with measurements of oxygen diffusion in undoped ZnO as a function of the oxygen pressure [12,13]. Moore and William [12] have observed a p_{O_2} dependence with $n = +1/2$, which corresponds to an oxygen diffusion mechanism by means of oxygen interstitial with null effective charge as shown in Table 1. This oxygen diffusion mechanism is predicted by Eq. (6).

On the other hand, Hoffman and Lauder [13] have found negative values for n, which should correspond to oxygen diffusion by means of a vacancy mechanism according to Table 1. However, the more recent works [2,6] on oxygen diffusion in ZnO have shown no experimental evidence for a vacancy mechanism.

It is worth noting that the works of Moore and Williams, and of Hoffman and Lauder, were performed using techniques assumed to be outdated [1]. Therefore, new experiments should be performed to confirm the dependence of the oxygen diffusion in ZnO with the oxygen pressure.

In conclusion, based on experimental data of oxygen diffusion and electrical conductivity measured in Al-doped ZnO, it is suggested that oxygen diffusion in zinc oxide occurs by means of an interstitial mechanism, with the interstitial oxygen having a null or a single negative effective charge. The identification of the correct value of the effective charge of the interstitial oxygen requires further confirmation through oxygen diffusion experiments as a function of the oxygen partial pressure in pure ZnO.

Table 1

Oxygen partial pressure dependence of the point defect concentration in ZnO for different electroneutrality conditions assuming an n-type semiconductor behaviour

Electroneutrality condition	Defects in zinc sublattice					Defects in oxygen sublattice						Electronic defects	
	$[Zn_i^\circ]$	$[Zn_i^{\circ\circ}]$	$[V_{Zn}^x]$	$[V_{Zn}']$	$[V_{Zn}'']$	$[O_i^x]$	$[O_i']$	$[O_i'']$	$[V_O^x]$	$[V_O^\circ]$	$[V_O^{\circ\circ}]$	$[e']$	$[h^\circ]$
$[Zn_i^\circ]=[e']$	$-1/4$	–	$1/2$	$1/4$	0	$1/2$	$1/4$	0	$-1/2$	$-1/4$	0	$-1/4$	$1/4$
$2[Zn_i^{\circ\circ}]=[e']$	–	$-1/6$	$1/2$	$1/3$	$1/6$	$1/2$	$1/3$	$1/6$	$-1/2$	$-1/3$	$-1/6$	$-1/6$	$1/6$
$[Al_{Zn}^\circ]=[e']$	$-1/2$	$-1/2$	$1/2$	$1/2$	$1/2$	$1/2$	$1/2$	$1/2$	$-1/2$	$-1/2$	$-1/2$	0	0

Acknowledgements

References

[1] G.W. Tomlins, J.L. Routbort, T.O. Mason, J. Am. Ceram. Soc. 81 (1998) 869.

[2] H. Haneda, I. Sakagushi, A. Watanabe, T. Ishigaki, J. Tanaka, J. Electroceram. 4 (S1) (1999) 41.

[3] T.K Gupta, W.G. Carlson, J. Mater. Sci. 20 (1985) 3487.

[4] T.K. Gupta, J. Am. Ceram. Soc. 73 (1990) 1817.

[5] H.L. Tuller, J. Eletroceram. 4 (S1) (1999) 33.

[6] A.C.S. Sabioni, M.J.F. Ramos, W.B. Ferraz, Mater. Res. 6 (2) (2003) 173–178.

[7] W.G. Carlson, T.K.J Gupta, J. Appl. Phys. 53 (1982) 5746.

[8] H. Yanagida, K. Koumoto, M. Miyayama, The Chemistry of Ceramics, Wiley, England, 1996.

[9] F.A. Kröger, The Chemistry of Imperfect Crystals, North-Holland, Amsterdam, Netherlands, 1974.

[10] J. Philibert, Atom Movements, Diffusion and Mass Transport in Solids, Les Editions de Physique, Les Ulis, France, 1991.

[11] M.A.N. Nogueira, W.B. Ferraz, A.C.S. Sabioni, Mater. Res. 6 (2) (2003) 167–171.

[12] W.J. Moore, E.L. William, Diffusion of zinc and oxygen in zinc oxide, Crystal Imperfections and the Chemical Reactivity of Solids, The Faraday Society, Aberdeen, Scotland, 1959, pp. 86–93.

[13] J.W. Hoffman, I. Lauder, Trans. Faraday Soc. 66 (1970) 2346.