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Defect Structure of Zn-Doped ZnO

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A defect structure model has been proposed for Zn-doped ZnO. Two donors, a native donor Zn_i, and an unknown donor D, and a native acceptor, V_{Zn}, have been suggested as the major defects. The model does account for the experimentally determined relationship between the concentration of electrons and the partial pressure of Zn. The unknown donor could be frozen-in oxygen vacancy, V_O, which thermodynamically cannot be distinguished from a foreign donor.

I. Introduction

The defect structure of nonstoichiometric $Zn_{1+x}O$ has previously been discussed by Kröger (*1*) and Garrett (*2*). Since then low-temperature electrical transport measurements of systematically Zn-doped ZnO have been reported (*3*), utilizing ZnO crystals heat treated at temperatures up to 1000°C in controlled atmospheres of Zn, and in 1 atm Ar and 1 atm O_2 and quickly cooled to room temperature. Electrical resistivity and Hall effect measurements were carried out at 77 to 370°K, and the concentration of electrons at room temperature n_{RT} was shown as functions of $\log p_{Zn}$ at constant T (p_{Zn} is the partial pressure of Zn and T is the temperature at the high-temperature annealing treatment).

From the cited experimental data, a defect structure model for ZnO can be inferred. Based on this model, a prediction of the zinc pressure and temperature dependence of the electron concentration in pure ZnO will be made.

II. Defect Structure Model

The two phase–two component system solid ZnO and its vapor has two degrees-of-freedom chosen as p_{Zn} and T. Consequently, the thermodynamic variables p_{Zn} and T control the defect structure of ZnO, and thus, the physical properties of ZnO.

At present, there is no direct evidence for the identity of all the defects in ZnO. However, based on the findings from the previous paper (*3*), the following observations can be made: (a) At high values of p_{Zn} and at constant T, $\log n \sim \frac{1}{3}\log p_{Zn}$ (see Kröger (*1*)), indicating a doubly ionized native donor. (b) A crystal quenched from this range exhibits at low temperature a shallow donor level (0.03–0.04 eV), indicating a singly ionized donor. (c) At intermediate values of p_{Zn} and at constant T, $\log n$ seems to be independent of p_{Zn}, indicating a frozen-in donor. (d) A crystal quenched from this intermediate range of p_{Zn} exhibits a shallow donor, i.e., singly ionized donor at low temperature. (e) A crystal quenched from annealing conditions with low values of p_{Zn}, for example 800°C in 1 atm of O_2 ($p_{Zn} = 1.6 \times 10^{-3}$ atm), exhibits a deep donor level, more than 0.165 eV below the conduction band, at low temperatures.

The observations a and b suggest that the native donor is interstitial zinc, Zn_i, with two *s*-electrons and may behave as an "$1s^2$" type donor with two ionization levels. At high temperature, values of 0.05 and 0.15 eV for the first and second ionization level are used. The

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native donor also could be an oxygen vacancy, but because of the rapid diffusion during the doping experiments, it seems more logical to choose interstitial zinc.

Observation c suggests a frozen-in donor D. Observations d and e suggest that this donor also has two ionization levels. Observation (e) also suggests that an acceptor defect is present. The fact that the electron concentration starts to decrease at lower p_{Zn} indicates the presence of a native acceptor assumed to be zinc vacancies V_{Zn}.

As a result, the following 11 species will be considered: e, electron in conduction band; h, hole in valence band; Zn_i^{x}, $\mathrm{Zn}_i^{\cdot}$, and $\mathrm{Zn}_i^{\cdot\cdot}$, interstitial zinc, neutral singly and doubly ionized; D^{x}, $D^{\cdot}$, and $D^{\cdot\cdot}$, unknown donor, neutral singly and doubly ionized; and V_{Zn}^{x}, V'_{Zn}, and V''_{Zn}, zinc vacancy, neutral singly and doubly ionized.

The resulting equilibrium equations are given in Table I. The values of the corresponding equilibrium constants are derived in the Appendix and listed in Table II. There are 11 dependent variables, and three independent variables, the total donor concentration $[D_T]$, p_{Zn}, and T. The problem is solved using the ten equations in Table I plus

$$[D^{x}] + [D^{\cdot}] + [D^{\cdot\cdot}] = [D_T] \tag{1}$$

and the neutrality condition

$$[e] + [V'_{\mathrm{Zn}}] + 2[V''_{\mathrm{Zn}}] = [h] + [\mathrm{Zn}_i^{\cdot}] + 2[\mathrm{Zn}_i^{\cdot\cdot}] + [D^{\cdot}] + 2[D^{\cdot\cdot}]. \tag{2}$$

TABLE I

CHEMICAL EQUILIBRIA AND CORRESPONDING MASS ACTION RELATIONS

	Equilibrium	Mass action relation
(I.1)	$\mathrm{Zn}_{\mathrm{Zn}} + \mathrm{O}_{\mathrm{O}} \rightleftharpoons \mathrm{Zn(g)} + \frac{1}{2}\mathrm{O_2(g)}$	$p_{\mathrm{Zn}}p_{\mathrm{O}_2}^{1/2} = K_{\mathrm{ZnO}}$
(I.2)	$\mathrm{Zn}_{\mathrm{Zn}} \rightleftharpoons \mathrm{Zn(g)} + V_{\mathrm{Zn}}^{x}$	$p_{\mathrm{Zn}}[V_{\mathrm{Zn}}^{x}] = K_{\mathrm{Zn}}$
(I.3)	$\mathrm{Zn(g)} \rightleftharpoons \mathrm{Zn}_i$	$[\mathrm{Zn}_i]/p_{\mathrm{Zn}} = K_{\mathrm{Zn}_i}$
(I.4)	$\mathrm{O} \rightleftharpoons e + h$	$[e][h] = K_i$
(I.5)	$V_{\mathrm{Zn}}^{x} \rightleftharpoons V'_{\mathrm{Zn}} + h$	$[V'_{\mathrm{Zn}}][h]/[V_{\mathrm{Zn}}^{x}] = K_{a1}$
(I.6)	$V'_{\mathrm{Zn}} \rightleftharpoons V''_{\mathrm{Zn}} + h$	$[V''_{\mathrm{Zn}}][h]/[V'_{\mathrm{Zn}}] = K_{a2}$
(I.7)	$\mathrm{Zn}_i^{x} \rightleftharpoons \mathrm{Zn}_i^{\cdot} + e$	$[\mathrm{Zn}_i^{\cdot}][e]/[\mathrm{Zn}_i^{x}] = K_{\mathrm{Zn}_{i1}}$
(I.8)	$\mathrm{Zn}_i^{\cdot} \rightleftharpoons \mathrm{Zn}_i^{\cdot\cdot} + e$	$[\mathrm{Zn}_i^{\cdot\cdot}][e]/[\mathrm{Zn}_i^{\cdot}] = K_{\mathrm{Zn}_{i2}}$
(I.9)	$D^{x} \rightleftharpoons D^{\cdot} + e$	$[D^{\cdot}][e]/[D^{x}] = K_{d1}$
(I.10)	$D^{\cdot} \rightleftharpoons D^{\cdot\cdot} + e$	$[D^{\cdot\cdot}][e]/[D^{\cdot}] = K_{d2}$

TABLE II

THE EQUILIBRIUM CONSTANTS $K = a\exp(-b/KT)$

		a	b(eV)
I.1	K_{ZnO}	$1.5 \times 10^{10}\ (\mathrm{atm})^{3/2}$	4.89
I.2	K_{Zn}	$1.33 \times 10^{30}\ (\mathrm{cm}^{-3}, \mathrm{atm})$	6.75
I.3	K_{Zn_i}	$1.04 \times 10^{19}\ (\mathrm{cm}^{-3}, \mathrm{atm}^{-1})$	0.68
I.4	K_i	$9.26 \times 10^{30}\ T^3\ (\mathrm{cm}^{-6})$	$3.343 – 8 \times 10^{-4}\ T$
I.5	K_{a1}	$2.33 \times 10^{16}\ T^{3/2}\ (\mathrm{cm}^{-3})$	0.8
I.6	K_{a2}	$5.83 \times 10^{15}\ T^{3/2}\ (\mathrm{cm}^{-3})$	2.8
I.7	$K_{\mathrm{Zn}_{i1}}$	$1.59 \times 10^{15}\ T^{3/2}\ (\mathrm{cm}^{-3})$	0.05
I.8	$K_{\mathrm{Zn}_{i2}}$	$3.97 \times 10^{14}\ T^{3/2}\ (\mathrm{cm}^{-3})$	0.15
I.9	K_{d1}	$1.59 \times 10^{15}\ T^{3/2}\ (\mathrm{cm}^{-3})$	0.05
I.10	K_{d2}	$3.97 \times 10^{14}\ T^{3/2}\ (\mathrm{cm}^{-3})$	0.15

To find $[e]$ as function of p_{Zn}, the dependent variables are expressed as function of $[D_T]$, p_{Zn}, T, and $[e]$. Thus,

$$[\mathrm{Zn}_i{}^x] = K_{\mathrm{Zn}_i} p_{\mathrm{Zn}} \tag{3}$$

$$[V^x_{\mathrm{Zn}}] = K_{\mathrm{Zn}} \frac{1}{p_{\mathrm{Zn}}} \tag{4}$$

$$[h] = K_i \frac{1}{[e]} \tag{5}$$

$$[V'_{\mathrm{Zn}}] = \frac{K_{a1} K_{\mathrm{Zn}}}{K_i} \frac{[e]}{p_{\mathrm{Zn}}} \tag{6}$$

$$[V''_{\mathrm{Zn}}] = \frac{K_{a1} K_{a2} K_{\mathrm{Zn}}}{K_i} \frac{[e]^2}{p_{\mathrm{Zn}}} \tag{7}$$

$$[\mathrm{Zn}_i{}^{\cdot}] = K_{\mathrm{Zn}_i} K_{\mathrm{Zn}_{i1}} \frac{p_{\mathrm{Zn}}}{[e]} \tag{8}$$

$$[\mathrm{Zn}_i^{\cdot\cdot}] = K_{\mathrm{Zn}_i} K_{\mathrm{Zn}_{i1}} K_{\mathrm{Zn}_{i2}} \frac{p_{\mathrm{Zn}}}{[e]^2}. \tag{9}$$

Using Eq. (1) and Eq. (I.9) and (I.10) in Table I, we find

$$[D^x] = \frac{[D_T]}{1 + (K_{d1}/[e]) + (K_{d1} K_{d2}/[e]^2)} \tag{10}$$

$$[D^{\cdot}] = \frac{[D_T]}{1 + (K_{d1}/[e]) + (K_{d1} K_{d2}/[e]^2)} \frac{K_{d1}}{[e]} \tag{11}$$

$$[D^{\cdot\cdot}] = \frac{[D_T]}{1 + (K_{d1}/[e]) + (K_{d1} K_{d2}/[e]^2)} \frac{K_{d1} K_{d2}}{[e]^2}. \tag{12}$$

By substituting for the variables in the neutrality equation. an expression is obtained for $[e]$

$$\begin{aligned}[e] = \Bigg(&K_i + K_{\mathrm{Zn}_i} K_{\mathrm{Zn}_{i1}} p_{\mathrm{Zn}} \\ &+ 2K_{\mathrm{Zn}_i} K_{\mathrm{Zn}_{i1}} K_{\mathrm{Zn}_{i2}} \frac{p_{\mathrm{Zn}}}{[e]} \\ &+ \frac{[D_T]}{1 + (K_{d1}/[e]) + (K_{d1} K_{d2}/[e]^2)} K_{d1} \\ &+ \frac{2[D_T]}{1 + (K_{d1}/[e]) + (K_{d1} K_{d2}/[e]^2)} \\ &\times \frac{K_{d1} K_{d2}}{[e]}\Bigg)^{1/2} \times \Bigg(1 + \frac{K_{a1} K_{\mathrm{Zn}}}{K_i} \cdot \frac{1}{p_{\mathrm{Zn}}} \\ &+ \frac{2K_{a1} K_{a2} K_{\mathrm{Zn}}}{K_i} \frac{[e]}{p_{\mathrm{Zn}}}\Bigg)^{-1/2}.\end{aligned} \tag{13}$$

The value for $[e]$ is solved by a simple iteration method using a computer.

III. Results and Discussion

The calculated values are compared with the experimental data in Fig. 1, where the relationship log$n$ versus logp_{Zn} is shown at 1000°C. A total donor concentration $[D_T] = 1 \times 10^{16}$ cm^{-3} has been assumed. The major defects are also shown. It was assumed that n at high temperatures simply is $2n_{RT}$, where n_{RT} is the room temperature value.

According to the proposed model, there are three ranges to consider: (a) At low zinc pressures the electron concentration increases with zinc pressure due to a decrease of the concentration of acceptors. (b) At intermediate zinc pressures the electron concentration is constant and equal to a frozen-in donor (native or foreign). (c) At high zinc pressures the electron concentration is increasing with the increasing native donor concentration.

In Fig. 2 are shown log$n$ versus $1/T$ plots at high temperatures for the three cases corresponding to the three ranges mentioned above: (1) in saturated zinc condition; (2) in argon gas where $p_{\mathrm{Zn}} = 2p_{\mathrm{O}_2}$ or also called the minimum pressure condition; and (3) in 1 atm of oxygen. The experimental points

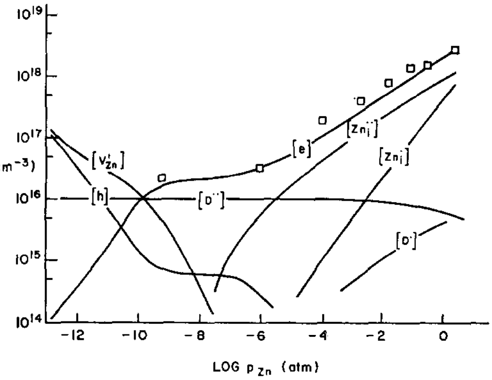

FIG. 1. The calculated concentrations of the major defects in ZnO are shown as function of the Zn-pressure at 1000°C. The experimental points are from (3). A frozen-in donor, $N_{\mathrm{D}} = 10^{16}$ cm^{-3} has been assumed.

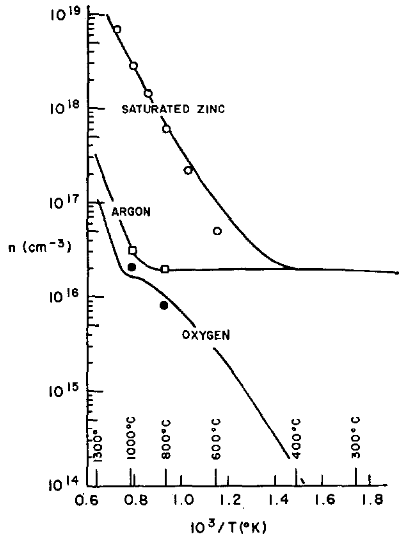

Fig. 2. The calculated concentration of electrons is shown as function of $1/T$ at three different conditions: in Zn-saturated conditions, in argon gas and in 1 atm of oxygen gas. The experimental points are from (3). The concentration of a frozen-in donor, $N_D = 10^{16}$ cm^{-3}.

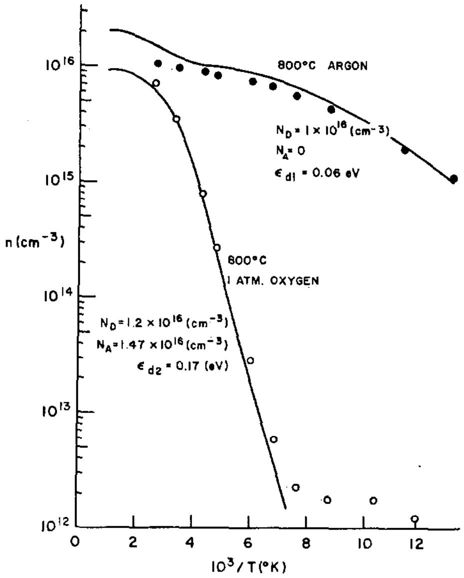

Fig. 3. The concentration of electron as function of $1/T$ at 373 to 77°K after being quenched from heat treatment at 800°C in argon or in 1 atm of oxygen. Only a slight change in concentration of acceptors results in drastic change in log n versus $1/T$.

are also shown and the agreement is fairly good.

The state of the semiconductor at room temperature will depend on from which one of these three ranges it has been cooled. From range 1, the low zinc pressure range, the crystal is compensated and the acceptor concentration $[A]$ is close to the donor concentration $[D]$. Thus, at low temperature, a deeper donor level will be exposed. If cooled from range 2, intermediate zinc pressures, the semiconductor is less dominated by the acceptors and the Fermi level will be closer to the conduction band. Consequently, a more shallow donor level will be exposed. This is illustrated in Fig. 3, where log$n$ versus $1/T$ at 77 to 300°K is shown for two cases: (a) crystal quenched from 800°C in O_2 (range 1) and (b) crystal quenched from 800°C in Ar (range 2). The donor concentration is very close to the same in both cases. Only the acceptor concentration is different. In the compensated case, the acceptor concentration is high enough to empty the shallow donor level; thus, the deeper donor level is exposed. In the present calculation this is assumed to be the second ionization of the same donor.

The nature of this donor is not known. A good fit to the experimental data is obtained by assuming $[D_T] \approx 10^{16}$ cm^{-3} for most of the ZnO crystals. The unknown donor could either be a foreign donor or a frozen-in native donor such as an oxygen vacancy. Pohl (4) has reported on irreversible changes in properties of ZnO crystal heated to high temperatures. This could possibly support the hypothesis of frozen-in oxygen vacancies. It has been shown that frozen-in native defects thermodynamically cannot be distinguished from foreign defects. All the crystals used in the previous study (3) were grown at fairly identical conditions and spark source mass spectrometric data did not suggest a specific impurity. Thus, it is not unlikely that the crystals will have a similar concentration of frozen-in oxygen vacancies. This is consistent with the data of Moore and Williams (5) who found that Zn_i diffuses much more rapidly than V_O in the temperature range in question. Recently, Hoffman and

Lauder (*6*) questioned the previous diffusion data, so obviously more information is needed to resolve the controversy. Also, a more detailed study of the defects would be necessary to determine the nature of the donor and to confirm the present hypothesis.

At high zinc pressures, range 3, the electron concentration is increasing with the native donor concentration according to

$$\log n \sim \tfrac{1}{3}\log p_{\mathrm{Zn}}.$$

This is consistent with studies of other II–VI compounds; see for example Hershman and Kröger (*7*), Callister, Varotto, and Stevenson (*8*), and Smith (*9*). In their cases, the electrical transport measurements were actually carried out at the high temperatures, whereas the present data were obtained at toom temperature on ZnO crystals quenched from high temperatures.

The present defect structure model differs from Kröger's (*1*) suggested model mainly in the choice of the major native defect (Kröger suggested V_{O}) and in the presence of an unknown donor that seems inherently to be present in vapor phase grown crystals. Otherwise, our data are in agreement with Kröger's tabulated values. Garrett (*2*) only considered one singly ionized donor (also Zn_i).

IV. Summary

A defect structure model has been proposed for ZnO to explain previously reported electrical transport property measurements. Two donors, a native donor Zn_i, and an unknown donor D, and a native acceptor V_{Zn}, have been suggested as the major defects. The model accounts for the experimentally determined relationship log n versus $\log p_{\mathrm{Zn}}$ fairly well. The unknown donor could be frozen-in oxygen vacancy V_{O}, which thermodynamically cannot be distinguished from a foreign donor.

Obviously, the relationship $\log n_{RT}$ versus $\log p_{\mathrm{Zn}}$ at constant T cannot lead to a conclusive picture of the nature of the defects involved. More direct physical measurements, such as EPR and optical studies, correlated with transport measurement (electrical and diffusion) are still needed in order to obtain a complete description of ZnO.

Appendix I. Evaluation of Equilibrium Constants

In Table I are listed 10 reactions with the corresponding equilibrium constants of the form

$$K = a\exp\left(-\frac{b}{kT}\right). \tag{A.1}$$

Kröger (*1*) has calculated parameters a and b for the various equilibrium constants near 1350°K based on earlier data. Values of some equilibrium constants are adjusted to make the theoretical results consistent with the recent electrical transport property data (*3*).

1. K_{ZnO} is related to the dissociation of ZnO. Kröger's values for a and b are used.

2. The equilibrium constants for the first and second ionization of a donor is

$$K_{d2} = \frac{1}{\beta_d} N_C \exp\left(-\frac{\varepsilon_{d1}}{kT}\right) \tag{A.2}$$

and

$$K_{d1} = \beta_d N_C \exp\left(-\frac{\varepsilon_{d2}}{kT}\right); \tag{A.3}$$

where β_d is the spin degeneracy of the donor the density of states of the conduction band is $N_C = 4.83 \times 10^{15}\ ((m_e^x/m)T)^{3/2}$; m_e^x is the density of states mass of electrons; m is the free electron mass; and ε_d is the donor level, subscripts 1 and 2 referring to first and second ionization.

Similar expression may be written for the acceptor:

$$K_{a1} = \frac{1}{\beta_a} N_V \exp\left(-\frac{\varepsilon_{a1}}{kT}\right) \tag{A.4}$$

and

$$K_{a1} = \beta_a N_V \exp\left(-\frac{\varepsilon_{a2}}{kT}\right), \tag{A.5}$$

where the symbols have similar meaning except that they apply to holes ionized into the valence band.

For a donor (acceptor) with two electrons (holes).

$$\beta_d = \beta_a = 0.5,$$

Kröger's values $\varepsilon_{a1} = 0.8$ eV, $\varepsilon_{a2} = 2.8$ eV, and $\varepsilon_{d1} = 0.05$ eV are utilized in the calculations except, to be consistent with the recent electrical transport data (*3*), for $\varepsilon_{d2} = 0.15$ eV. The values $m_e^x = 0.3\,m$ and $m_h^x = 1.8\,m$ are taken from Neuberger (*10*).

3. The equilibrium constant K_i is related to the excitation of electrons from the valence into the conduction band and is expressed by

$$K_i = N_C N_V \exp\left(-\frac{E_G}{kT}\right) \qquad (A.6)$$

where the band gap of ZnO (*10*) $E_G = 3.343 - 8 \times 10^{-4}\,T$.

The resulting values for the *a*'s and *b*'s are listed in Table II.

4. The equilibrium constant K_{Zn} is related to the equilibrium

$$Zn_{Zn} = Zn(g) + [V_{Zn}^x]. \qquad (A.7)$$

K_{Zn} is chosen such that $[V_{Zn}'] = 1 \times 10^{16}$ (cm^{-3}) at $T = 800°C$ and $p_{O_2} = 1$ atm in accordance with the electrical transport measurements (*3*).

From Table I and using Eq. (I.1), (I.2), (I.4), and (I.5), it can be seen that

$$K_{Zn} = \frac{K_i K_{ZnO}}{K_{a1}} \frac{]V_{Zn}']}{[e]p_{O_2}{}^{1/2}} \qquad (A.8)$$

or for $[e] \approx [V_{Zn}'] = 1 \times 10^{16}$ (cm^{-3}), $p_{O_2}^{1/2} = 1$ atm,

$$K_{Zn} = \beta_a N_C\, 1.5 \times 10^{10} \exp\left(-\frac{6.58}{kT}\right) \qquad (A.9)$$

or

$$K_{Zn} = 5.95 \times 10^{24} T^{3/2} \exp\left(-\frac{6.58}{kT}\right). \qquad (A.10)$$

By using, as suggested by Kröger (*1*),

$$T^3 = 5 \times 10^{10} \exp\left(-\frac{0.34}{kT}\right), \qquad (A.11)$$

$$K_{Zn} = 1.33 \times 10^{30} \exp\left(-\frac{6.75}{kT}\right) (cm^{-3}, atm). \qquad (A.12)$$

The parameters *a* and *b* are listed in Table II.

5. The equilibrium constant K_{Zn_i} is related to the equilibrium

$$Zn(g) = Zn_i. \qquad (A.13)$$

K_{Zn_i} is adjusted such that the calculated [*e*] agrees with the experimental results (*3*) at saturated Zn conditions;

$$[e]_{sat} = 2n_{RT} = 5.36 \times 10^{21} \exp\left(-\frac{0.83}{kT}\right) cm^{-3} \qquad (A.14)$$

assuming that the electron concentration at high temperatures is twice the room temperature value.

Experimentally it was also found (see *3*) that at constant *T*

$$\log n \sim \tfrac{1}{3} \log p_{Zn},$$

indicating that a doubly ionized donor is involved. Because of the rapid in-diffusion of donors during the Zn doping, donors are assumed to be zinc interstitials rather than oxygen vacancies. As a result the following neutrality condition is satisfied.

$$[e]_{sat} = 2[Zn_i^{\cdot\cdot}] + [Zn_i^{\cdot}]. \qquad (A.15)$$

From Eq. (I.3), (I.7), and (I.8) in Table I

$$K_{Zn_i} = \frac{[e]_{sat}^3}{2K_{Zn_{i1}} K_{Zn_{i2}} p_{Zn} + K_{Zn_{i1}} p_{Zn}[e]} \qquad (A.16)$$

where $[e]_{sat}$ is given in Eq. (A.14) and the vapor pressure of zinc is (*11*)

$$p_{Zn} = 1.66 \times 10^5 \exp\left(-\frac{1.22}{kT}\right) (atm). \qquad (A.17)$$

By substituting for the parameters in Eq. (A.16)

$$K_{Zn_i} \approx 1.04 \times 10^{18} \exp\left(-\frac{0.68}{kT}\right) (cm^{-3}, atm). \qquad (A.18)$$

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