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Calculation of Carrier Electron Concentration in ZnO Depending on Oxygen Partial Pressure

Eun-Dong Kim, Jong-Mun Park, Sang-Cheol Kim, and Nam-Kyun Kim
Power Semiconductor Research Group, Korea Electrotechnology Research Institute
P. O. Box 20, Changwon, 641-600 Gyoungnam, Republic of Korea

ABSTRACT

The relationship between carrier electron concentration(n) and atmosphere oxygen partial pressure(P_{O_2}) for pure ZnO calculated by the mass-action law, well-known as $n \propto P_{O_2}^{-1/m}$ where $m = 4$ or 6 for the single or the double ionization of the native donor defects due to its nonstoichiometry, respectively, is found in competition with the calculation result on the basis that the total defect concentration is the sum of those of unionized and ionized defects. Definitively, it is found inconsistent with the calculation result by employing the Fermi-Dirac(FD) statistics for their ionization processes.

By application of the FD statistics law to the ionization while assuming the defect formation is still ruled by the mass-action law, the calculation results shows the concentration is proportional to $P_{O_2}^{-1/2}$ whenever they ionize singly and/or doubly.

Conclusively we would like to propose the new theoretical relation $n \propto P_{O_2}^{-1/2}$ because the ionization processes of donors in ZnO should be treated with the electron-occupation probability at localized quantum states in its forbidden band created by the donor defects, i.e. the FD statistics.

1. INTRODUCTION

ZnO has been well-known as one of important oxide semiconductor materials, actively used for electronic devices such as displays, electrical surge protection devices, gas sensors, and so on[1-4]. ZnO materials obtained at experimentally attainable atmospheres always exhibit extrinsic n-type conductivity at room temperature even without impurity doping. It was also found that ZnO is one of famous nonstoichiometry materials, always characterized by metal excess. The nonstoichiometry of metal excess might result from interstitial zinc (Zn_i) and/or oxygen vacancy (V_O), which can donate electron(s) into the conduction band of the host crystal ZnO at room temperature. Therefore it is generally recognized that the n-type conductivity of pure ZnO is responsible for the native donor defects due to its nonstoichiometry. Some text books[7-10] treat ZnO as a good example for understanding the defect electrochemistry. Recently the existence and importance of zinc vacancy have been suggested[5,6] as recommending ZnO as green-color emission phosphor for cathode ray tube and field emission display.

It becomes more important for device and process engineers to exactly understand the relationships between defect science and electrical properties for designing and fabricating better devices. Modern statistical thermodynamics treats the impurity ionization process in solids as the electron-occupation process at its localized quantum

state(s) in the forbidden band gap of host crystal, i.e. with the FD statistics law[16].

Defect electrochemistry in silicon has been very extensively investigated, which has convinced us of the feasibility of the FD law. No one can deny the great contribution of the FD statistics to the remarkable progress in the present semiconductor industry.

The mass-action law is, however, still used to calculate the relationships among carrier concentrations and atmosphere vapor pressures of constituents for compound semiconductors with nonstoichiometry such as ZnO and NiO[12]. The mass law considers the ionization processes of such point defects as chemical reaction between electron and defect masses. In some cases the application of the mass-action law to impurity ionization has seemed suitable to explain experimental results so far. But one can find inconsistency between the calculation result for ZnO from the modem semiconductor theory based on the FD statistics and the ordinary understanding based on the law of mass action as seen in the text books[7,8] and review papers[11,12]. It is really surprising that the incompatibility has not been found in spite of the importance of ZnO in modern electronic devices even so far.

In this work, a new relationship between carrier electron concentration and oxygen partial pressure will be proposed by employing the FD statistics for the ionization processes of native donor defects Zn_i and V_O while the formation of the defects is assumed still governed by the mass law.

In this work the effect of zinc vacancy on the carrier concentration will not be considered, because its ionization energy was found much higher than that of donor defect even though the Schottky or Frenkel disorder would make the vacancy[11]. Its effect on the carrier concentration will be discussed in a coming paper.

The authors would like to expect that this proposal could provide a clue to better understanding for the electrochemistry of the defects due to the nonstoichiometry in ZnO and could help developing better ZnO devices.

2. REVIEW OF THE CALCULATIONS BY THE MASS-ACTION LAW

2.1. DEFECT FORMATION BY THE NONSTOICHIOMETRY

If we put $[Zn]/[O]=1+x$, we can define x as the nonstoichiometry coefficient, where [ ] denotes concentration. Several experiments revealed that x is larger than 0 for pure ZnO under experimentally attainable atmospheres, which implies that its nonstoichiometry is responsible for zinc excess or oxygen deficiency.

(1) Zinc Interstitial Model

The interstitial zinc in a zinc-excessive ZnO crystal, Zn_i, can positively ionize to be a donor donating electron(s) to its conduction band at room temperature. High vapor pressures of zinc can produce the interstitial zinc in ZnO crystal lattice;

$$Zn(g)\ \square\ Zn_i, \qquad (1)$$

$$K_i=[Zn_i]_{T,P}\cdot P_{Zn}^{-1}, \qquad (2)$$

where K_i is the equilibrium reaction constant of the mass-action relation describing the Zn_i formation, $[Zn_i]_{T,P}$ the thermal equilibrium concentration of the interstitial defect under the formation condition, and P_{Zn} the partial pressure of atmosphere zinc vapor.

P_{Zn} vs. P_{O_2} relation can be defined from the formation reaction of ZnO;

$$Zn(g) + 1/2O_2 \;\square\; ZnO. \quad (3)$$

The mass-action law related to the Henry's law gives the equilibrium constant of the formation reaction, K_{ZnO};

$$K_{ZnO} \cong P_{Zn}^{-1} \cdot P_{O_2}^{-1/2}. \quad (4)$$

According to Eqs. (2) and (4), the defect concentration is approximated to

$$[Zn_i]_{T,P} = K_i / K_{ZnO} \cdot P_{O_2}^{-1/2}. \quad (5)$$

Classical thermodynamics[7] found that, if this reaction takes place at T_R in K, the equilibrium constant can be given as a function of the reaction temperature as follows;

$$K(T_R) = K^0 \cdot \exp(-\Delta S^0 / kT_R) \cdot \exp(-\Delta H^0 / kT_R) \quad (6)$$

where K^0 is a constant, ΔS^0 the entropy change, ΔH^0 the enthalpy change, and k the Boltzmann constant.

(2) Oxygen Vacancy Model

Since oxygen vacancy V_O in oxides was found able to donate electron(s) to its conduction band, one can choose the oxygen vacancy model as an alternative defect model for explaining the n-type conductivity of pure ZnO. Oxygen in a normal lattice site O_O can be removed by reduction atmosphere, remaining a vacancy at the lattice oxygen site;

$$O_O \;\square\; V_O + 1/2O_2. \quad (7)$$

If the reaction equilibrium constant K_V for the above mass-action relation is known, one can obtain

$$[V_O]_{T,P} = K_V \cdot P_{O_2}^{-1/2} \quad (8)$$

where $[V_O]_{T,P}$ is the vacancy concentration under the condition of (T_R, P_{O_2}). This model shows the same P_{O_2}-dependence as the interstitial model does. Therefore it is clear that the donor defect concentration in ZnO is proportional to $P_{O_2}^{-1/2}$ whatever the kind of major donor defect is. The major one among the native donor defects should be determined mainly by the magnitude of ΔH^0 for defect formation at a given condition[11]. By Eq. (4), we can express $[V_O]_{T,P}$ as a function of P_{Zn}, which means that the vacancy as well as the interstitial zinc can be made under the same atmosphere.

2.2. CALCULATION OF THE ELECTRON CONCENTRATION

As the measurement of electron concentration is conducted at temperatures low enough to make the donor defects immovable in the ZnO crystal lattice like room temperature, resulting in no reactions such as atom diffusion, the impurity concentration will remain constant during the measurement. If the mass law would be acceptable to the defect ionization under all conditions, it should be applicable for the assumed condition. In this work we will make our calculation with this condition for interpretation convenience.

(1) Single Ionization

If the activation energy for the double (or second) ionization of the interstitial is much higher than the thermal energy kT_m corresponding to the measuring temperature T_m it is not necessary to consider the double ionization. The ionization reaction of interstitial zinc can be expressed with the mass-action relation at the temperature T_m;

$$Zn_i^{\times} \ \square \ Zn_i^{\bullet} + \text{e}. \tag{9}$$

Its equilibrium constant, K_{SZ}, will be described by

$$K_{SZ} = n \cdot [Zn_i^{\bullet}]/[Zn_i^{\times}] \tag{10}$$

where $Zn_i^{\bullet}$ and $Zn_i^{\times}$ are the singly ionized and unionized interstitials, respectively.

When there are no other impurities ionized and the donor concentration is much higher than the intrinsic hole concentration, $[Zn_i^{\bullet}] \gg p$, the charge neutrality gives

$$n \cong [Zn_i^{\bullet}]. \tag{11}$$

Therefore one can obtain the electron concentration as a function of P_{O_2} from Eqs. (5), (10) and (11), as follows;

$$n = \sqrt{K_i \cdot K_{SZ} / K_{ZnO}} \cdot P_{O_2}^{-1/4} \tag{12}$$

when we put $[Zn_i]_{T,P} = [Zn_i^{\times}]$ [11].

The text books[7,8] concluded that the single ionization model is preferred since the calculation result from the single ionization model, $n \propto P_{O_2}^{-1/4}$, was in good agreement with the results of the experimental conductivity measurement, $\sigma \propto P_{O_2}^{-1/4}$. We have to, however, keep in mind that the conclusion is disputable because the P_{O_2}-dependence of σ is not always responsible for that of carrier density because σ can be influenced by the electron mobility μ_e which can be affected by the ionized impurity concentration. Furthermore researchers should more carefully consider the experimental variables affecting the conductivity such as electrical barriers due to the ionized impurity concentration distribution at the semiconductor surface region[11] and the Schottky effect at metal/ZnO contact[14,15].

If the formation and the ionization enthalpy of the oxygen vacancy are much smaller than those of the interstitial zinc, the electron concentration is approximated to

$$n = \sqrt{K_V \cdot K_{SV}} \cdot P_{O_2}^{-1/4} \tag{13}$$

because the charge carrier, i.e. the conduction electron, would be given by the ionization mass relation of the vacancy with the equilibrium reaction constant K_{SV};

$$V_O^{\times} \ \square \ V_O^{\bullet} + \text{e}. \tag{14}$$

(2) Double Ionization

Different electrical conductivity data taken as a function of zinc partial pressure[9] indicated that the predominant donor species is a doubly ionized native defect. Since the mass-action relation for the second ionization of Zn_i can be described as

$$Zn_i^{\bullet} \ \square \ Zn_i^{\bullet\bullet} + \text{e}, \tag{15}$$

therefore the equilibrium constant is given by

$$K_{DZ} = n \cdot [Zn_i^{\bullet\bullet}]/[Zn_i^{\bullet}]. \tag{16}$$

Using Eqs. (10) and (16) with the charge neutrality approximated to $n \cong 2[Zn_i^{\bullet\bullet}]$ when most of the defects are doubly ionized, the electron density is

$$n = (K_i \cdot K_{SZ} \cdot K_{DZ} / 2K_{ZnO})^{1/3} \cdot P_{O_2}^{-1/6}. \tag{17}$$

One can obtain the same P_{O_2}-dependence of n even in the vacancy model as the above equation. Calculation results for all the models are summarized in Table 1.

Table 1. Variation of the P_{O_2}-dependence of electron concentration with models of defect and ionization for ZnO of nonstoichiometry, calculated by the mass-action law.

Defect Model	Ionization	Ionization Reaction Constant	Charge Neutrality	Electron Concentration
Interstitial Zinc	Single	$K_{SZ} = n \cdot [Zn_i^{\bullet}]/[Zn_i^{\times}]$	$n \cong [Zn_i^{\bullet}]$	$n \square P_{O_2}^{-1/4}$
	Double	$K_{SZ} \cdot K_{DZ} = n^2 \cdot [Zn_i^{\bullet\bullet}]/[Zn_i^{\times}]$	$n \cong 2[Zn_i^{\bullet\bullet}]$	$n \square P_{O_2}^{-1/6}$
Oxygen Vacancy	Single	$K_{SV} = n \cdot [V_O^{\bullet}]/[V_O^{\times}]$	$n = [V_O^{\bullet}]$	$n \square P_{O_2}^{-1/4}$
	Double	$K_{SV} \cdot K_{DV} = n^2 \cdot [V_O^{\bullet\bullet}]/[V_O^{\times}]$	$n = 2[V_O^{\bullet\bullet}]$	$n \square P_{O_2}^{-1/6}$

In the calculations we assumed that Zn_i and V_O singly or doubly ionize in dichotomy. But we know that the ionization reaction is temperature-dependent and hence the single and the double ionization may be predominant at lower temperatures and at higher temperatures, respectively. Since the singly and doubly ionized donors can simultaneously exist at arbitrary temperatures the charge neutrality results in $n \square [Zn_i^{\bullet}] + 2[Zn_i^{\bullet\bullet}]$, which may give a quite different calculation result.

2.3. DISCUSSIONS ON THE APPLICATION LIMIT OF THE MASS LAW

If the calculations by application of the mass law to the donor ionization agreed with the results by the FD statistics, it would not be easy to deny the feasibility of the mass law in spite of Swalin's declaration[7], the mass-action law can not be compatible with the FD statistics. It is because some experimental results for ZnO have still seemed to support it. It is, however, note-worthy that Sukkar and Tuller[11] tried to apply the FD statistics but partly.

The calculations from the mass law have usually been made under the assumption of $[Zn_i]_{T,P} = [Zn_i^{\times}]$. Concentrations of $Zn_i^{\bullet}$ and electron are inter-dependent by the definition for the equilibrium constant in the mass law as seen in Eq. (10), while the total concentration of interstitial zinc, $[Zn_i]_{T,P}$, is no more a variable at the assumed measuring temperature because it was already determined by the defect formation condition (T_R, P_{O_2}) as seen in Eq. (5) and has remained unchanged during the measurement. If an infinitesimal amount of electrons (Δn) is injected by a suitable method into a ZnO crystal with the equilibrium concentration n, the reaction (7) will be forced into backward direction. It will result in the decrease of the ionized donor and the increase of the unionized. But this may be not occurred according to the FD statistics law because the number of ionized ions is determined by the FD distribution

function depending on ionization temperature regardless of the amount of the injected electrons. It is said that the ionized defect concentrations are 'self-controlled' for charge neutrality, which may not occur because the defect formation reaction can occur in neither forward nor backward direction at such a low temperature (T_m) we assumed. The charge neutrality can be rather established by the well-known relation $n \cdot p = n_i^2$. One could more easily recognize it by considering phosphor donor diffused into silicon.

Furthermore the interstitial zincs additionally neutralized by Δn, $\Delta[Zn_i^\times]$, should disturb the equilibrium of its formation reaction in Eq. (1), which expels it into backward direction, reaching a new equilibrium with a lower Zn_i concentration. Since $[Zn_i^\bullet]$ and n should be in equilibrium with $[Zn_i^\times]$ but not the total concentration $[Zn_i]_{T,P}$, it is not reasonable to put $[Zn_i^\times] = [Zn_i]_{T,P}$. After all we should put

$$[Zn_i^\times] = [Zn_i]_{T,P} - [Zn_i^\bullet]. \tag{18}$$

Then this will modify Eq. (12) as follows;

$$K_{SZ} = n \cdot [Zn_i^\bullet]/[Zn_i^\times] = n \cdot [Zn_i^\bullet]/([Zn_i]_{T,P} - [Zn_i^\bullet]). \tag{19}$$

This equation shows that the Eq. (12) is valid only at $[Zn_i]_{T,P} \gg [Zn_i^\bullet]$.

Sukkar and Tuller[9] introduced this concept only for the substituted donor(D_{Zn}) but not for the native defects such as Zn_i and V_O. The FD statistics was used for the ionization of the substituted defect but surprisingly the mass law was applied for the defects due to the nonstoichiometry. Although they were different donor species having different origins, their ionization processes should have been treated by the same manner.

By using Eq. (19), one can obtain

$$n = (\sqrt{K_{SZ}^2 + 4K_{SZ} \cdot K_i / K_{ZnO} \cdot P_{O_2}^{-1/2}} - K_{SZ})/2. \tag{20}$$

It is obvious that the above result is somewhat different from the previous calculation results, of cause, even though it results in $n \propto P_{O_2}^{-1/4}$ when $K_{SZ} \square 4K_i / K_{ZnO} \cdot P_{O_2}^{-1/2}$.

The double ionization model of Zn_i where $[Zn_i]_{T,P} = [Zn_i^\times] + [Zn_i^{\bullet\bullet}]$ gives

$$n^3 + K_{SZ} \cdot K_{DZ} \cdot n - 2K_i \cdot K_{SZ} \cdot K_{DZ} / K_{ZnO} \cdot P_{O_2}^{-1/2} = 0, \tag{21}$$

where the charge neutrality was given to $n \cong 2[Zn_i^{\bullet\bullet}]$.

Since the ionization reaction is affected by temperature even in the scope of the Boltzmann statistics, it is more reasonable to put $[Zn_i]_{T,P} = [Zn_i^\times] + [Zn_i^\bullet] + [Zn_i^{\bullet\bullet}]$ for an arbitrary ionization condition. That is, since an elevated temperature can give a finite probability that a singly ionized donor secondly ionizes to become a doubly ionized donor, ZnO may have not only $Zn_i^\bullet$ but also $Zn_i^{\bullet\bullet}$. Therefore the charge neutrality will be give to $n \square [Zn_i^\bullet] + 2[Zn_i^{\bullet\bullet}]$ for a generalized ionization condition where $p \square [Zn_i^\bullet] + 2[Zn_i^{\bullet\bullet}]$. Then the relationship between n and P_{O_2} is given as

$$n^3 + K_{SZ} \cdot n^2 + K_{SZ}(K_{DZ} - K_i / K_{ZnO} \cdot P_{O_2}^{-1/2}) \cdot n - 2K_{SZ} \cdot K_{DZ} \cdot K_i / K_{ZnO} \cdot P_{O_2}^{-1/2} = 0. \tag{22}$$

Indeed our calculation based on the mass law, Eq. (22), shows the slope value of $\partial \ln n$ *vs.* $\partial \ln P_{O_2}$ plot is not a constant but a complicated and continuous function of temperature. Earlier experimental results, showing $\partial \ln n / \partial \ln P_{O_2} = -1/4$ or $-1/6$ even

in a temperature range, does not agree with the above calculation based on the mass law, which make us wonder if the mass law is valuable for the defect ionization or not.

If the measurement is made at an elevated temperature of which the equivalent thermal energy kT_m is larger than the ionization energy of Zn_i but much less than its formation energy, the concentration of native defects already formed at (T_R, P_{O_2}) must remain unchanged during the measurement. This case results in $n = [Zn_i^{\bullet}] = [Zn_i]_{T,P}$ for the single ionization model and $n = 2[Zn_i^{\bullet\bullet}] = 2[Zn_i]_{T,P}$ for the double ionization, which implies that the electron concentration may be proportional to $P_{O_2}^{-1/2}$ regardless of the ionization valence state. Therefore it is clear that there needs a new approach for smart explanation of the defect ionization.

3. CALCULATION BY APPLICATION OF THE FERMI-DIRAC STATISTICS

The electron density in phosphor-doped n-type Si, for example, is calculated not by the mass law but by application of the FD statistics law. No one can find any reason to specially treat the native donor defects in pure ZnO unlike the phosphor donor in Si. Therefore ionization processes of all defects in ZnO should also be governed by the FD statistics. Their formation processes would, however, be still ruled by the law of mass action because not only it has been found to represent these types of chemical formation reactions very well but also no alternative ways can more precisely interpret the defect formation processes than this.

In general the electron-occupation probability at a donor state of a potential level E_D can be calculated by the FD distribution function[14];

$$f_{FD}(E_D) = N_{DU} / N_D = [1 + g^{-1} \cdot \exp\{(E_D - E_F)/kT\}]^{-1}, \qquad (23)$$

where N_{DU} is the concentration of the occupied donor with electron meaning the unionized donor, N_D its total concentration, g the spin degeneracy of the donor level, and E_F the Fermi energy. If the total donor concentration N_D is known, one can very easily calculate the ionized donor density N_{DI} by using the above equation without aid of the mass law as follows;

$$N_{DI} = N_D - N_{DU} = \{1 - f_{FD}(E_D)\} \cdot N_D = [1 + g \cdot \exp\{-(E_D - E_F)/kT\}]^{-1} \cdot N_D. \qquad (24)$$

In the application of the FD statistics, it is not reasonable to consider the single and the double ionization process separately. But, in this work, separated considerations for the two will be tried for easy comparison with the previous results.

3.1. Considering Only the Single Ionization

Let's start our calculation with the interstitial model under the assumption that $[Zn_i]_{T,P}$ was already determined with the formation condition (T_R, P_{O_2}) and then the concentration, $[Zn_i]_{T,P} = K_i / K_{ZnO} \cdot P_{O_2}^{-1/2}$, remains unchanged during this concentration measurement at T_m. If the interstitial zinc has only one ionization state at energy level E_i within the forbidden band of ZnO, the concentration of ionized interstitial $Zn_i^{\bullet}$ can be obtained by using Eq. (24) as;

$$[Zn_i^{\bullet}]=\{1-f_{FD}(E_i)\}\cdot[Zn_i]_{T,P}=[1+g\cdot\exp\{-(E_i-E_F)/kT_m\}]^{-1}\cdot K_I(T_R)\cdot P_{O_2}^{-1/2}, \quad (25)$$

where $K_I(T_R)=K_i^0/K_{ZnO}^0\cdot\exp\{(\Delta S_{ZnO}^0-\Delta S_i^0)/kT_R\}\cdot\exp\{(\Delta H_{ZnO}^0-\Delta H_i^0)/kT_R\}$.

If there are no ionized acceptors the charge neutrality gives $n=p+[Zn_i^{\bullet}]$, then

$$n=n_i^2/n+[Zn_i^{\bullet}], \quad (26)$$

where $n_i=4.9\times10^{15}(m_e^{\bullet}\cdot m_h^{\bullet}/m_0^2)^{3/4}\cdot T_m^{3/2}\cdot\exp(-E_g/2kT_m)$, $m_e^{\bullet}$ and $m_h^{\bullet}$ are the effective electron and hole masses, respectively, and m_0 the free-electron mass at rest[15]. Since $n^2-[Zn_i^{\bullet}]\cdot n-n_i^2=0$ from the above equation, one can obtain n as a function of P_{O_2};

$$n=[K_I(T_R)\cdot\{1-f_{FD}(E_i)\}\cdot P_{O_2}^{-1/2}+\sqrt{K_i^2(T_R)\cdot\{1-f_{FD}(E_i)\}^2\cdot P_{O_2}^{-1}+4n_i^2}\,]/2, \quad (26)$$

Highly doped n-type ZnO might be in the condition of $[Zn_i^{\bullet}]\Box p$ and it can be approximated to

$$n\Box[Zn_i^{\bullet}]=[1+g\cdot\exp\{-(E_D-E_F)/kT_m\}]^{-1}\cdot K_I(T_R)\cdot P_{O_2}^{-1/2}. \quad (27)$$

This shows that the dependence of n on P_{O_2} calculated by application of the FD statistics to the ionization, $n\Box P_{O_2}^{-1/2}$, is quite different from the result by the mass law, n $\Box P_{O_2}^{-1/4}$, for the same single ionization model of the interstitial zinc.

3.2 Considering the Second Ionization

It seems from several experimental results[17-20] that the interstitial zinc makes two ionization states at 0.02~0.05eV and 0.2~0.5eV below the bottom of ZnO conduction band. The outermost energy level and the next outer one of interstitial zinc atom will make the first and second quantum states localized in the forbidden band of the host crystal ZnO, respectively. Fig. 1 shows possible ionization ways the zinc atom at the interstitial site of ZnO crystal lattice, creating two quantum states beneath the bottom of its conduction band, can have. The first and second quantum states of Zn_i are defined to be located below E_{i1} and E_{i2} from the bottom of the conduction band, respectively, because of uncertainty in the determination of their exact values.

One can find four cases of ionization an interstitial zinc can have; (a) both the two quantum states(E_{i1} and E_{i2}) are filled with electron, (b) the first quantum state(E_{i1}) is empty while the second state(E_{i2}) is filled, (c) the first state filled while the second state empty, and (d) the two states empty.

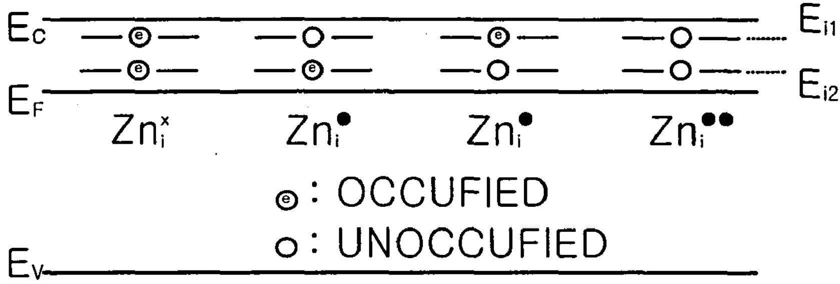

Fig. 1. Schematic illustration for possible ionization ways the interstitial zinc can have in ZnO, which has two ionization states, E_{i1} and E_{i2}, in the forbidden band beneath the conduction band edge of the host ZnO crystal

The case (a) is corresponding to the unionization of Zn_i, the cases (b) and (c) are responsible for the single ionization, and finally the case (d) for the double ionization. But the single ionization in the mass law included only the case (b). There was no need to consider the second ionization reaction in the calculation of singly ionized donor density by the mass law but now one can know that it must be taken into account in the calculation by the FD statistics as the case (c) indicates. Unfortunately there is no way to take the case (c) into account without considering the case (b) in the mass law as the previous calculation procedure has shown. In other words, the electron release from the second state always implies the double ionization in the mass law but in the viewpoint of the FD statistics it does not always imply the double ionization.

Since the probability for the case (b) is $\{1-f_{FD}(E_{i1})\}\cdot f_{FD}(E_{i2})$ and that of the case (c) is $f_{FD}(E_{i1})\cdot\{1-f_{FD}(E_{i2})\}$, the concentration of the singly ionized defect is given as

$$[Zn_i^\bullet]=f_{FD}(Zn_i^\bullet)\cdot[Zn_i]_{T,P}=f_{FD}(Zn_i^\bullet)\cdot K_I(T_R)\cdot P_{O_2}^{-1/2}, \quad (28)$$

where $f_{FD}(Zn_i^\bullet)=\{1-f_{FD}(E_{i1})\}\cdot f_{FD}(E_{i2})+f_{FD}(E_{i1})\cdot\{1-f_{FD}(E_{i2})\}$. The concentration is again proportional to $P_{O_2}^{-1/2}$ in the case of the single ionization including the case (c).

Since the probability for the two states to be simultaneously empty is $f_{FD}(Zn_i^{\bullet\bullet})=\{1-f_{FD}(E_{i1})\}\cdot\{1-f_{FD}(E_{i2})\}$, the concentration of the doubly ionized donor is

$$[Zn_i^{\bullet\bullet}]=f_{FD}(Zn_i^{\bullet\bullet})\cdot[Zn_i]_{T,P}=f_{FD}(Zn_i^{\bullet\bullet})\cdot K_I(T_R)\cdot P_{O_2}^{-1/2}. \quad (29)$$

This reveals that even $[Zn_i^{\bullet\bullet}]$ is also proportional to $P_{O_2}^{-1/2}$.

In general a nontoichiometric ZnO crystal with interstitial zinc will simultaneously have both $Zn_i^\bullet$ and $Zn_i^{\bullet\bullet}$ at arbitrary temperatures. Then the carrier concentration is

$$n \,\square\, [Zn_i^\bullet]+2[Zn_i^{\bullet\bullet}]=\{f_{FD}(Zn_i^\bullet)+2f_{FD}(Zn_i^{\bullet\bullet})\}\cdot K_I(T_R)\cdot P_{O_2}^{-1/2}, \quad (30)$$

where $f_{FD}(Zn_i^\bullet)+2f_{FD}(Zn_i^{\bullet\bullet})=\{1-f_{FD}(E_{i1})\}+\{1-f_{FD}(E_{i2})\}$. This result still support n is proportional to $P_{O_2}^{-1/2}$.

From these results, it can be considered that the electron concentration is proportional to $P_{O_2}^{-1/2}$ for the interstitial model whenever it ionizes singly and/or doubly. One can

find the same result of $n \propto P_{O_2}^{-1/2}$ for the oxygen vacancy model.

The value of $\partial \ln n / \partial \ln P_{O_2}$ from the mass law should vary with temperature. There have been no experimental evidences for it. It is noteworthy that the value in the FD statistics law does not vary with temperature.

4. CONCLUSION

The dependence of carrier electron concentration on atmosphere oxygen partial pressure for ZnO crystal, pure but of nonstoichiometry, was reviewed with application of the mass-action law. The concentration of donor defect(s) due to its nonstoichiometry was clearly proportional to $P_{O_2}^{-1/2}$.

The mass law seemed to support that the electron concentration n is proportional to $P_{O_2}^{-1/4}$ for the single ionization of the donor defect(s) and $P_{O_2}^{-1/6}$ for the double ionization whatever the major donor defect is, which resulted from the assumption of $[Zn_i^{\times}] = [Zn_i]_{T,P}$ or $[V_O^{\times}] = [V_O]_{T,P}$.

We showed it more reliable to put $[Zn_i^{\times}] = [Zn_i]_{T,P} - [Zn_i^{\bullet}]$ or $[V_O^{\times}] = [V_O]_{T,P} - [V_O^{\bullet}]$ for the single ionization model but $[Zn_i^{\times}] = [Zn_i]_{T,P} - [Zn_i^{\bullet\bullet}]$ or $[V_O^{\times}] = [V_O]_{T,P} - [V_O^{\bullet\bullet}]$ for the double ionization. These definitions result in different relationships between n and P_{O_2} in comparison with the well-known expressions.

Since the ionization in a generalized condition, i.e. at arbitrary temperatures, results in $[Zn_i]_{T,P} = [Zn_i^{\times}] + [Zn_i^{\bullet}] + [Zn_i^{\bullet\bullet}]$ and $n \cong [Zn_i^{\bullet}] + 2[Zn_i^{\bullet\bullet}]$ in the interstitial model, which approximately gives $\ln n \propto -1/m \cdot \ln P_{O_2}$ where m is a continuous function of temperature varying with ionization temperature at $4 \leq m \leq 6$.

Earlier experimental results have seemed to support the relationship $n \propto P_{O_2}^{-1/m}$ with a constant m-value, 4 or 6, but they cannot agree with the modified relationship having m variable with temperature under the generalized condition. Therefore it is worthwhile to consider an alternative way to describe the impurity ionization in ZnO. Modern semiconductor physics shows that the ionization of phosphor donor in silicon crystal should be treated by the FD statistics but not with the mass law. It is rather reasonable to consider the native defects in ZnO due to its nonstoichiometry with the same way as quantum solid-state physics deals with defects of silicon.

By application of the FD statistics to the ionization while assuming the formation of defects is still ruled by the mass action law, the calculation results showed the electron concentration is proportional to $P_{O_2}^{-1/2}$ whatever the donor defect is and whenever it ionizes singly and/or doubly.

Consequently we would like to propose the new theoretical relation $n \propto P_{O_2}^{-1/2}$ because the ionization process of donors in ZnO should be treated with the electron-occupation probability at localized quantum states in its forbidden band created by the donor defects, i.e. the FD statistics.

The authors are looking forward to many discussions can trim the calculation and precise experiments can approve the reliability of the calculation result.

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