Effect of Zinc Vacancy on Carrier Concentrations of Nonstoichiometric ZnO

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Abstract

We proposed that concentrations of carrier electron as well as ionized donor defects in nonstoichiometric ZnO are proportional to $P_{O_2}^{-1/2}$, whenever they ionizes singly or doubly, by employing the Fermi-Dirac (FD) statistics for ionization of the native thermal defects Zn_i and V_O. The effect of acceptor defect, zinc vacancy V_{Zn} made by the Frenkel and Schottky disorder reactions, on carrier concentrations was discussed. By application of the FD statistics law to their ionization while the formation of defects is assumed governed by the mass-action law, the calculation results indicate; 1. ZnO shows n-type conductivity with $N_D > N_A$ and majority concentration of $n \propto P_{O_2}^{-1/2}$ in a range of P_{O_2} lower than a critical value. 2. As the concentration of acceptor V_{Zn} increases proportional to $P_{O_2}^{1/2}$, ZnO made at extremely high P_{O_2} can have p-type conductivity with majority concentration of $p \propto P_{O_2}^{1/2}$. One may not, however, obtain p-type ZnO if the pressure for $N_D < N_A$ is too high.

Key Words: ZnO, nonstoichiometric, defect, FD statistics, O_2 partial pressure, mass-action law

1. INTRODUCTION

ZnO has been studied for piezoelectric devices[1,2]. ZnO materials obtained at experimentally attainable atmospheres always exhibit extrinsic n-type conductivity even without impurity doping. It was also found that ZnO is one of famous nonstoichiometric 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.

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[3]. 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 modern semiconductor theory based on the FD statistics and the ordinary understanding based on the law of mass action as seen in the text book[4] and review papers[3,5]. 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.

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2. FORMATION OF DEFECTS IN ZnO

2.1. Formation of ZnO

ZnO can be made by oxidation of zinc vaporized from its molten metal;

$$Zn(g) + \tfrac{1}{2}O_2 = ZnO \quad (1)$$

The law of mass action gives the equilibrium constant of the reaction at T_R, $K_{ZnO}(T_R)$[3] is given as

$$K^0_{ZnO}\cdot\exp(-\Delta S_{ZnO}/kT_R)\cdot\exp(-\Delta H_{ZnO}/kT_R)=P_{Zn}^{-1}\cdot P_{O_2}^{-1/2} \quad (2)$$

where K° is a constant, ΔS° the entropy change, ΔH° the enthalpy change, k the Boltzmann constant, and P the partial pressure.

2.2. Formation of Native Defects by the Nonstoichiometry

Most experiments for pure ZnO revealed that it has the nonstoichiometry of [Zn]/[O]≥1 under experimentally attainable conditions, which might be responsible for zinc

excess or oxygen deficiency, where [] denotes concentration.

High vapor pressures of zinc can produce the interstitial zinc in ZnO crystal lattice;

$Zn(g) \square Zn_i$ ....(3)

$K_i(T_R) = [Zn_i]_{T_R} \cdot P_{Zn}^{-1}$ ....(4)

where $[Zn_i]_{T_R}$ is the thermal equilibrium concentration of the interstitial defect. According to Eqs. (2) and (4), the defect concentration is described by

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

Oxygen in a normal lattice site O_O can be removed by reduction atmosphere, remaining a vacancy at the lattice oxygen site, V_O;

$O_O \square V_O + \frac{1}{2}O_2$ ....(6)

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

$[V_O]_{T_R} = K_V(T_R) \cdot P_{O_2}^{-1/2}$ ....(7)

This model shows the same P_{O_2}-dependence as the interstitial model. Therefore it is clear that the thermal equilibrium concentration of native donor defects is proportional to $P_{O_2}^{-1/2}$ whatever the kind of major donor defect is.

2.3. Formation of Native Defects by Disorder

Various experimental data suggest that the Frenkel disorder in ZnO is predominant at lower temperatures but the Schottky disorder becomes increasingly important at higher temperatures.[5] The Frenkel disorder is given as follows;

$Zn_{Zn} \square Zn_i + V_{Zn}$ ....(8)

the equilibrium constant of the disorder reaction is

$K_F(T_R) = [Zn_i][V_{Zn}]$ ....(9)

Therefore the vacancy concentration by the Frenkel disorder, $[V_{Zn}]_F$, is given by

$K_F(T_R) \cdot [Zn_i]_{T_R}^{-1} = \{K_F(T_R) \cdot K_{ZnO}(T_R)/K_i(T_R)\} \cdot P_{O_2}^{1/2}$ ....(10)

The anti-Frenkel disorder in the anion site, $O_O = O_i + V_O$, will need a much higher Gibbs free energy change because of its larger ionic radius than zinc. Then we ignore it.

The Schottky disorder is also given as;

$null = V_{Zn} + V_O$ ....(11)

$[V_{Zn}]_S = K_S(T_R) \cdot [V_O]_{T_R}^{-1} = \{K_S(T_R)/K_V(T_R)\} \cdot P_{O_2}^{1/2}$ ....(12)

Since the zinc vacancy concentration is mainly determined by the magnitude of $\Delta H_{V_{Zn}}$, the contribution of the Schottky disorder on its concentration cannot be ignored even though ΔH_S is lager than ΔH_F.

3. CALCULATION OF CARRIER CONCENTRATION BY THE FD STATISTICS

The author maintains that the ionization of defects in ZnO as well as all solid materials should be treated not by the mass action law but by the viewpoint of the quantum statistical thermodynamics, as the electron-occupation problem in localized quantum state(s) in the forbidden band gap of host crystal made by them. The mass law deals with the defect ionization as a chemical reaction between electron and defect masses.

We assume that the ionization of all defects in ZnO is governed by the FD statistics but their formation reactions would be still ruled by the law of mass action.

For an acceptor impurity with the ionization energy level of E_A, the electron capture probability of the acceptor state, the ionization probability, is given by

$f_{FD}^A(E_A) = N_{AI}/N_A = [1 + g \cdot \exp\{(E_A - E_F)/kT\}]^{-1}$ .....(13)

where N_{AI} is the concentration of acceptors occupied by electron meaning the ionized acceptor, N_A its total concentration, and g the spin degeneracy of the acceptor level.

3.1. Concentration of Ionized Donor

Several experimental results[6,7] showed 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.

From Fig. 1, one can see the quantum states of Zn_i in the forbidden band gap of ZnO. The first and second states of Zn_i, ${}^1Zn_i$ and ${}^2Zn_i$, are defined to be located beneath the bottom edge of the conduction band, respectively.

One can find four cases of ionization for an interstitial zinc in Fig. 2. 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

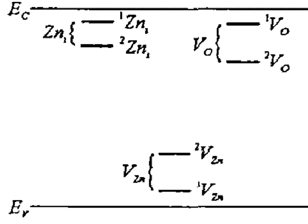

Fig. 1. Energy States of Zn_i, V_O, and V_{Zn} in the band gap of ZnO. Real values of the states are not exactly known.[4)]

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 $\{1-f_{FD}^{D}({}^{1}Zn_i)\}\cdot f_{FD}^{D}({}^{2}Zn_i)$ and that of the case (c) is $f_{FD}^{D}({}^{1}Zn_i)\cdot\{1-f_{FD}^{D}({}^{2}Zn_i)\}$, the concentration of the singly ionized defect is given as

$$[Zn_i^{\bullet}] = f_{FD}^{D}(Zn_i^{\bullet})\cdot[Zn_i]_{T_R} = f_{FD}^{D}(Zn_i^{\bullet})\cdot K_I(T_R)\cdot P_{O_2}^{-1/2} \quad (14)$$

where

$$f_{FD}^{D}(Zn_i^{\bullet}) = \{1-f_{FD}^{D}({}^{1}Zn_i)\}\cdot f_{FD}^{D}({}^{2}Zn_i) + f_{FD}^{D}({}^{1}Zn_i)\cdot\{1-f_{FD}^{D}({}^{2}Zn_i)\}$$

The relation equation shows that the concentration is proportional to $P_{O_2}^{-1/2}$, contrary to the calculation result from the mass law, $\propto P_{O_2}^{-1/4}$.

Since the probability for the two states to be simultaneously empty is $f_{FD}^{D}(Zn_i^{\bullet\bullet})=\{1-f_{FD}^{D}({}^{1}Zn_i)\}\cdot\{1-f_{FD}^{D}({}^{2}Zn_i)\}$, the concentration of the doubly ionized donor is

$$[Zn_i^{\bullet\bullet}] = f_{FD}^{D}(Zn_i^{\bullet\bullet})\cdot[Zn_i]_{T_R} = f_{FD}^{D}(Zn_i^{\bullet\bullet})\cdot K_I(T_R)\cdot P_{O_2}^{-1/2} \quad (15)$$

This reveals that $[Zn_i^{\bullet\bullet}]$ 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 charge concentration ($N_{Zn_i}^{+}$)is

$$[Zn_i^{\bullet}]+2[Zn_i^{\bullet\bullet}]=\{1-f_{FD}^{D}({}^{1}Zn_i)\cdot f_{FD}^{D}({}^{2}Zn_i)\}\cdot K_I(T_R)\cdot P_{O_2}^{-1/2} \quad (16)$$

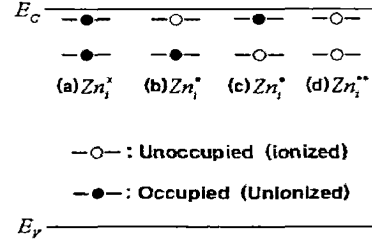

Fig. 2. Illustration of ionization methods of the interstitial zinc with two donor states beneath the conduction band edge of ZnO.

This result indicates that the concentration is proportional to $P_{O_2}^{-1/2}$, quite different from the calculation result from the mass law.

By the same manner as above, one can calculate the concentration of singly ionized oxygen vacancy $V_O^{\bullet}$;

$$[V_O^{\bullet}] = f_{FD}^{D}(V_O^{\bullet})\cdot[V_O]_{T_R} = f_{FD}^{D}(V_O^{\bullet})\cdot K_V(T_R)\cdot P_{O_2}^{-1/2} \quad (17)$$

where

$$f_{FD}^{D}(V_O^{\bullet}) = \{1-f_{FD}^{D}({}^{1}V_O)\}\cdot f_{FD}^{D}({}^{2}V_O) + f_{FD}^{D}({}^{1}V_O)\cdot\{1-f_{FD}^{D}({}^{2}V_O)\}.$$

We assume that the vacancy has two states in donor level, ${}^{1}V_O$ and ${}^{2}V_O$.

The concentration of doubly ionized donor $V_O^{\bullet\bullet}$ is given by

$$[V_O^{\bullet\bullet}] = f_{FD}^{D}(V_O^{\bullet\bullet})\cdot[V_O]_{T_R} = f_{FD}^{D}(V_O^{\bullet\bullet})\cdot K_V(T_R)\cdot P_{O_2}^{-1/2} \quad (18)$$

where $f_{FD}^{D}(V_O^{\bullet\bullet}) = \{1-f_{FD}^{D}({}^{1}V_O)\}\cdot\{1-f_{FD}^{D}({}^{2}V_O)\}$.

Then the total charge concentration ($N_{V_O}^{+}$) is

$$[V_O^{\bullet}]+2[V_O^{\bullet\bullet}] = \{1-f_{FD}^{D}({}^{1}V_O)\cdot f_{FD}^{D}({}^{2}V_O)\}\cdot K_V(T_R)\cdot P_{O_2}^{-1/2} \quad (19)$$

Even though a kind of native donor defects has a formation energy value larger than that of another kind, the fact does not means that the former defect cannot be created but it has a lower concentration. Therefore the total concentration of positively ionized charges is given by

$$N_D^{+} = [Zn_i^{\bullet}]+2[Zn_i^{\bullet\bullet}]+[V_O^{\bullet}]+2[V_O^{\bullet\bullet}] = Kf_D\cdot P_{O_2}^{-1/2} \quad (20)$$

where

$$Kf_D=\{1-f_{FD}^{D}({}^{1}Zn_i)\cdot f_{FD}^{D}({}^{2}Zn_i)\}\cdot K_I(T_R)+\{1-f_{FD}^{D}({}^{1}V_O)\cdot f_{FD}^{D}({}^{2}V_O)\}\cdot K_V(T_R)$$

3.2. Conentration of Ionized Acceptor

Though the Gibbs free energy change of the Schottky disorder reaction is larger than that of the Frenkel disorder reaction at lower temperatures, it is more reasonable to take the defect concentration from the latter reaction into account. One cannot distinguish the defects from the Frenkel and Schottky disorders. Therefore the total zinc

vacancy concentration is given by

$$[V_{Zn}]_T = [V_{Zn}]_F + [V_{Zn}]_S = K_A(T_R) \cdot P_{O_2}^{1/2} \quad (21)$$

where

$K_A(T_R) = \{K_F(T_R) \cdot K_{ZnO}(T_R)/K_i(T_R)\} + \{K_S(T_R)/K_V(T_R)\}$.

The vacancies of divalent zinc site may have two acceptor levels, ${}^1V_{Zn}$ and ${}^2V_{Zn}$ regardless of their origin. Therefore the total charge density of ionized acceptors;

$$N_A^- = [V_{Zn}^{'}] + 2[V_{Zn}^{''}] = Kf_A \cdot P_{O_2}^{1/2} \quad (22)$$

where

$Kf_A = \{f_{FD}^A({}^1V_{Zn}) + f_{FD}^A({}^2V_{Zn}) - f_{FD}^A({}^1V_{Zn}) \cdot f_{FD}^A({}^2V_{Zn})\} \cdot K_A(T_R)$

It shows that the negatively charged acceptor density is proportional to $P_{O_2}^{1/2}$ contrary to the case of the donor density.

3.3. Carrier Concentration

At lower oxygen partial pressures ($P_{O_2} << Kf_D/Kf_A$), N_D^+ might be much large than N_A^- and the intrinsic hole concentration p. From the charge neutrality equation, one can obtain

$$n \cong Kf_D \cdot P_{O_2}^{-1/2} \quad (23)$$

When $P_{O_2} >> Kf_D/Kf_A$, that is, at very high oxygen partial pressures, ZnO can have p-type conductivity because of $N_A^- >> N_D^+$. The majority carrier, hole, concentration is approximated to

$$p \cong Kf_A \cdot P_{O_2}^{1/2} \quad (24)$$

The real concentrations of carriers are expressed by

$$n = \{Kf_D \cdot P_{O_2}^{-1/2} - Kf_A \cdot P_{O_2}^{1/2} + \sqrt{(Kf_D \cdot P_{O_2}^{-1/2} - Kf_A \cdot P_{O_2}^{1/2})^2 + 4n_i^2}\}/2$$

$$p = \{Kf_A \cdot P_{O_2}^{1/2} - Kf_D \cdot P_{O_2}^{-1/2} + \sqrt{(Kf_A \cdot P_{O_2}^{1/2} - Kf_D \cdot P_{O_2}^{-1/2})^2 + 4n_i^2}\}/2$$

where $n_i = 4.9 \times 10^{15} \cdot (m_{de} \cdot m_{dh}/m_0^2)^{3/4} \cdot T^{3/2} \cdot \exp(-E_g/kT)$.

The concentrations of carriers are plotted in Fig. 3 as functions of P_{O_2} compared with those of imperfections.

The critical oxygen pressure for $N_D = N_A$, $[Zn_i] + [V_O] = [V_{Zn}]_T$, is given by

$$P_{O_2}(\text{I}) = \frac{K_i \cdot K_V(K_i + K_V \cdot K_{ZnO})}{K_{ZnO}(K_F \cdot K_V \cdot K_{ZnO} + K_i \cdot K_S)} \quad (25)$$

If this value is too high or beyond solidus line in $P-T$ phase diagram of ZnO, one cannot obtain p-type ZnO. Furthermore, since the ionization energies of the acceptor V_{Zn} are much higher than those of donors Zn_i and V_O, as shown in Fig. 2, the condition for $p = n$ comes at higher P_{O_2} as seen in Fig. 3. This implies it rather difficult to make p-type ZnO.

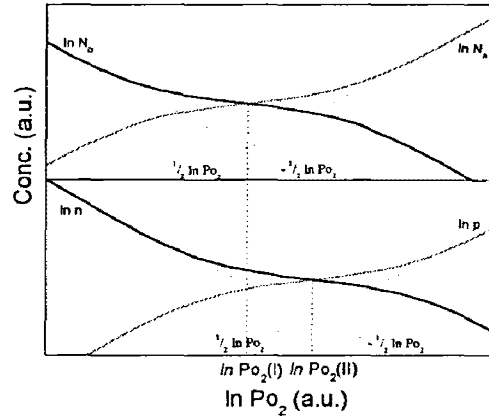

Fig. 3. Concentrations of carriers and defects as functions of P_{O_2}.

4. CONCLUSION

The dependence of carrier concentrations on atmosphere oxygen partial pressure for ZnO crystal, pure but of nonstoichiometry, have been reviewed with application of the mass-action law for formation of native thermal defects while the FD statistics for their ionization.

Our calculations confirm that the concentration of donor defect(s) due to its nonstoichiometry is inversely proportional to $P_{O_2}^{1/2}$ and that of acceptor due to is directly proportional to $P_{O_2}^{1/2}$ as known. This implies that ZnO has the n-type conductivity with majority carrier concentration of approximate $n \propto P_{O_2}^{-1/2}$ for lower oxygen pressures as well known but p-type ZnO with $p \propto P_{O_2}^{1/2}$ can be made at extremely high P_{O_2}. But one cannot obtain it if the condition for $N_A > N_D$ is beyond solidus line in P-T phase diagram of ZnO.

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