Calculation of Formation Energy of Oxygen Vacancy in ZnO Based on Photoluminescence Measurements

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The formation energy of an oxygen vacancy in ZnO was calculated. The photoluminescence intensity of green emission was used as a measure of vacancy concentration, and its variation as a function of reduction temperature was monitored. This enabled a thermodynamic approach based on experimental data, which is in contrast with most previous studies, which focused on a theoretical treatment based on first principles methods. Two reduction conditions were used: hydrogen gas flow and a CO/CO2 atmosphere generated using activated carbon. The two cases were compared, and mechanisms for the formation of oxygen vacancies during thermal treatment were investigated. The similar results obtained for the two cases indicate that the proposed models of VO formation are reasonable.

1. Introduction

Zinc oxide (ZnO) has generated much interest because of its potential use in various applications including semiconductor devices, transparent conducting oxides, chemical and gas sensors, surface acoustic wave devices, and ultraviolet (UV) emitters.1–3 ZnO has also been investigated as a phosphor material for display devices because it shows strong green emission after thermal treatment in a reducing atmosphere. Defects such as Cu-related impurities,4 interstitial zinc or oxygen atoms (Zni or Oi),5–7 surface oxygen defects,8–10 oxygen antisites (Oi),11 and oxygen vacancies (VO)12–18 are considered to be possible causes of this photoluminescence (PL). Although the exact mechanism remains a matter of discussion, many research groups concur that the green emission originates from oxygen vacancies.

Many researchers have calculated the formation energy of oxygen vacancies.13,19–25 Most calculations are based on a theoretical approach using first principles methods. However, the results are inconsistent: the reported values for the formation of a neutral vacancy vary depending on the method used for density functional theory (DFT) calculations. It is therefore important to obtain the formation energy experimentally and to compare it with theoretical values. This would provide a useful reference for correcting the parameters used in theoretical calculations.

In this study, we calculated the Gibbs free energy for the formation reaction of oxygen vacancies based on experimental measurements. The PL intensity of green emission was used as a measure of the vacancy concentration. To the best of our knowledge, this approach has never been attempted before. Two kinds of reduction conditions were used: hydrogen gas flow and a CO/CO2 atmosphere generated using activated carbon. The two cases were compared, and the formation mechanisms of oxygen vacancies during thermal treatment were investigated.

The self-consistency of the results confirms that oxygen vacancies are responsible for green emission from ZnO.

2. Experimental Methods

Commercial ZnO powder (Sigma Aldrich, 99.9%, < 5 µm) was heat-treated at various temperatures in one of two reducing atmospheres: mixed gas flow composed of 5% H2 and 95% N2 (Praxair, 99.9999%) and a CO/CO2 atmosphere produced using activated carbon (Junsei Chemicals). For reduction under gas flow, 2 g of ZnO powder was placed in an alumina boat and heated in a tube furnace with a diameter of 6 cm and a length of 60 cm. The mixed gas had a flow rate of 100 sccm after purging. Activated carbon was used to generate the CO/CO2 atmosphere. Carbon granules (50 g) were placed in a 250 mL crucible on which an alumina boat containing 2 g of ZnO powder was placed, and the crucible was capped. The crucible was then heated in a box furnace at temperatures between 450 and 1000 °C. The heating and cooling rates of the furnace were 15 °C/min, and the maximum temperature was maintained for 30 min.

The mass of the powder sample was monitored to determine mass loss during heating. The PL was measured using a Xe lamp and a monochromator system (Acton Research Corp.). The excitation light wavelength was fixed at 325 nm for emission measurement. The emission was amplified by a photomultiplier tube (PMT; Acton, PHV 400) prior to detecting the signal. Change in the maximum peak height of PL emission was monitored for a thermodynamic analysis of VO formation in ZnO crystals.

3. Results

The PL emission of untreated ZnO powder was very weak, but it could be enhanced by heating the powder in a reducing atmosphere. Reduction greatly increased the intensity of visible light, which has a peak at ~500 nm (Figure 1). The observation that both reducing atmospheres enhance the emission suggests that the formation of oxygen vacancies is responsible for the green emission.

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The Hertz-Knudsen equation,\textsuperscript{26} which describes the flux of molecules that evaporate from a condensed phase, is given as follows

\[
\frac{dN_e}{A_e \, dt} = \alpha_e (2\pi mkT)^{-1/2}(p^* - p)
\]

where \(N_e\) denotes the number of molecules evaporating from a condensed phase and \(A_e\) represents the surface area of the condensed phase, \(m\) is the mass of the gas molecule participating in the reaction, \(p^*\) is the equilibrium partial pressure of the evaporating material, and \(p\) is the actual partial pressure. \(\alpha_e\) is the evaporation coefficient, which is the ratio between the actual amount of evaporation and the theoretical maximum. This value is known to be affected by many factors, including the surface geometry, contamination, and microscopic reaction mechanisms.

The following reactions describe the formation of \(V_o\), which has a low concentration

\[
O_O^X + H_2(g) \leftrightarrow V_o^X + H_2O(g) \quad (1)
\]

\[
O_O^X + CO(g) \leftrightarrow V_o^X + CO_2(g) \quad (2)
\]

Equations 1 and 2 describe the process by which \(H_2\) and \(CO\) gas molecules react with oxygen atoms in the crystal to form \(V_o\). Oxygen evaporation may be driven only by a low oxygen partial pressure with no interaction between \(O_O\) and \(H_2\) or \(CO\).

To assess the likelihood of this possibility, we also performed the same procedure with a flow of ultra-pure nitrogen gas after sufficient purging, revealing only a slight increase in the green emission intensity. This result demonstrates that it is difficult to form \(V_o\) in the case that a reduction in the oxygen partial pressure is the only driving force and that \(V_o\) is not produced as a result of the spontaneous evaporation of \(O_O\) without interaction with other gas molecules. Therefore, models based on eqs 1 and 2 seem to be accurate.

Using the observed change in the green emission intensity, we performed a thermodynamic analysis of \(V_o\) formation in ZnO crystals using the Hertz-Knudsen equation. For a given set of conditions, it is possible to calculate \(p^*\), and the \(N_e\) flux can be estimated from the change in the number of \(V_o\), which is traced from the green emission intensity. Using these values and fitting the emission intensity as a function of the reduction temperature, \(p^*\) can be calculated. Finally, the Gibbs free energy of \(V_o\) formation can be evaluated.

In this procedure, the emission intensity is assumed to be a linear function of the number of \(V_o\). Figure 2 shows PL emission and excitation spectra for green emission. The green emission is excited mainly by UV radiation with wavelengths below 400 nm, and the PL emission and excitation spectra are sufficiently separated from each other. This shows that the resonance condition for energy transfer is not fulfilled. In addition, the lifetime of green emission is known to be very short. These optical characteristics mean that a nonradiative transition followed by excitation energy transfer is a difficult process in ZnO.\textsuperscript{27} Thus, the number of \(V_o\) may be assumed to be linearly proportional to the PL green emission intensity, which enables the emission intensity to be used to estimate the \(V_o\) and \(N_e\) concentrations.

### 3.1. Reduction under \(H_2/N_2\) Flow

Reaction 1 can be divided into the following three subreactions for the formation of \(V_o\)

\[
O_O^X \leftrightarrow V_o^X + O(g) \quad (1-1)
\]

\[
O(g) \leftrightarrow \frac{1}{2}O_2(g) \quad (1-2)
\]

\[
\frac{1}{2}O_2(g) + H_2(g) \leftrightarrow H_2O(g) \quad (1-3)
\]

The Hertz-Knudsen equation for reaction 1 is expressed as

**Figure 1.** PL emission spectra of ZnO samples after heat treatment. (a) Reduction in \(H_2/N_2\) gas flow and (b) reduction in a \(CO/CO_2\) atmosphere generated by activated carbon (\(\lambda_{ex} = 325\) nm).

**Figure 2.** PL excitation and emission spectra of ZnO powder reduced at 700 °C in \(H_2/N_2\) gas flow.
\[
\frac{dN_t}{d\tau} = \alpha_v(2\pi m_{H_{2}O}kT)^{1/2}(p_{H_{2}O}^{*} - p_{H_{2}O})
\] (3)

Under a continuous flow of 5% H\textsubscript{2}, \(p_{H_{2}O}^{*} + p_{H_{2}O} \approx 0.05\) atm, and \(p_{H_{2}O}\) can be assumed to be negligible. The Gibbs free energy can be expressed in terms of the equilibrium constant of reaction 1, and for the standard-state equilibrium, it can be written in the form \(\Delta G^\circ = A + BT\). Thus, eq 3 can be arranged as

\[
I = (C\alpha_v p_{H_{2}O}^{1/2})T^{1/2}
\left[\frac{0.05 \exp(-\frac{A + BT}{RT})}{1 + \exp(-\frac{A + BT}{RT})}\right]
\] (4)

where \(I\) is the emission intensity of green light and \(A, B,\) and \(C\) are constants that can be determined by fitting \(I\) as a function of temperature. Figure 3a shows experimentally measured data written as - Carbon. The reduction process by CO gas is expressed by reaction 1-1, can be calculated as

\[
\text{O}_4 \rightarrow \text{O}_6 \rightarrow \text{O}_0 + \text{O} (g), \quad \Delta G^\circ = 585900 - 204444 T \text{ (J/mol)}
\] (5)

3.2. Reduction in CO/CO\textsubscript{2} Atmosphere Using Activated Carbon. The reduction process by CO gas is expressed by reaction 2, for which the Hertz-Knudsen equation can be written as

\[
\frac{dN_t}{d\tau} = \alpha_v(2\pi m_{CO}kT)^{1/2}(p_{CO}^{*} - p_{CO})
\] (6)

\(p_{CO}\) and \(p_{CO_{2}}\) in the crucible were calculated from eq 7 below.\textsuperscript{29}

The partial pressure values were corrected by assuming equilibrium emission of gas.

\[
\text{CO} (g) + \frac{1}{2}\text{O}_2 (g) \rightarrow \text{CO}_2 (g), \quad \Delta G^\circ = -282400 + 8681 T \text{ (J/mol)}
\] (7)

The Hertz-Knudsen equation for reaction 2 can be modified in a similar manner as for hydrogen reduction. Whereas \(p_{H_{2}O}\) was ignored in eq 3 for hydrogen reduction, \(p_{CO}\) is significantly large, and it changes as a function of temperature. Therefore,

\[
I = (C\alpha_v p_{CO_{2}}^{1/2})T^{1/2}
\left[\frac{(p_{CO} + p_{CO_{2}}) \exp(-\frac{A + BT}{RT})}{1 + \exp(-\frac{A + BT}{RT})} - p_{CO_{2}}\right]
\] (8)

The experimental data and fitting results are presented in Figure 3b. Only the data below 825 °C were used for fitting. As for the hydrogen reduction case, emission in the high-temperature range had a lower intensity than that expected from eq 8. As mentioned above, this is attributed to a high defect concentration and rapid evaporation. The sample reduced at 1000 °C exhibited a large decrease in emission intensity, and its wavelength was red-shifted, which seems to be an extreme case of a defective structure.

The values of \(A, B,\) and \(C\) were estimated by fitting to be \(3.80 \times 10^4\) (J/mol), \(-28.3\) (J/mol·K), and \(2.90 \times 10^3\) respectively, and for reaction 2, the Gibbs free energy is calculated to be \(\Delta G^\circ = 3.80 \times 10^4 - 28.37 T\) (J/mol). Using the data for reaction 1-2 and eq 7, the Gibbs free energy for the \(V_O\) forming reaction is calculated to be

\[
\Delta G^\circ = A + BT
\]
4. Discussion

The Gibbs free energy for the formation of $V_O$ needs to be converted to electronvolts to enable a comparison with the results of DFT calculations performed by other research groups. The converted values are $6.064 - 2.11 \times 10^{-3}T(eV/N_{O(g)})$ for reduction under $H_2/N_2$ flow and $5.904 - 1.840 \times 10^{-3}(eV/\nu_{O})$ for the case of activated carbon. Similarity of the results obtained in the two cases indicates that the models for the $VO$ formation expressed in eqs 1 and 2 are reasonable. At 0 K, the Gibbs free energy is calculated to be $\approx 6$ eV; this is somewhat larger than the value arrived at by DFT calculations, which has been reported to be in the range of $3.5-5.5$ eV. This discrepancy arises because our calculation results are based on the standard state (i.e., 1 atm of O(g)), whereas DFT calculations usually assume two extreme cases: oxygen-poor and oxygen-rich conditions. Therefore, oxygen partial pressure needs to be modified to enable a comparison of the present results with the results of previous DFT calculations. If the oxygen is assumed to be a monatomic ideal gas, then the Gibbs free energy for the reduction process can be expressed in the form of $\Delta G^o + RT \ln \alpha_{0}(\nu_{O(g)})$, where $\alpha_{0}$ is the activity of the vacancy in ZnO. Because $\alpha_{0}$ is in the equilibrium concentration range of oxygen vacancies at a given temperature and $P_{\nu}(g)$ is very low in actual situations, the formation energy of oxygen vacancy, $\Delta G$, is smaller than 6 eV. This calculation could provide us the limiting value, 6 eV, for the formation energy of oxygen vacancy in ZnO.

Existing thermodynamic data for reactions $\text{ZnO} \rightarrow \nu \text{Zn} + \frac{1}{2} \nu \text{O}_2$ and $\nu \text{Zn} \rightarrow \nu \text{Zn} + \nu O$ can be combined to determine the enthalpy for the reaction $\text{ZnO} \rightarrow \nu \text{Zn} + \nu O$, giving a value of 709 ± 300 J/mol. This is slightly smaller than the value of $6 \times 10^3$ eV. Comparing these enthalpy values, the average number of O–Zn bonds broken to form one oxygen vacancy is estimated to be 3.304. This is smaller than the theoretical value of 4. (In a perfect crystal with a wurtzite structure, an oxygen atom becomes free when four Zn–O bonds are broken because it is coordinated with four zinc atoms.) This discrepancy may reflect the fact that the reaction occurs near the surface, where some of the oxygen atoms are exposed and already have broken bonds. An alternative explanation is a change in effective bonding energy at the surface; thus, additional systematic investigations may be necessary to determine the exact mechanism. For the CO case (reaction 2), the enthalpy was 570 ± 400 J/mol and the average number of bonds broken is calculated to be 3.217, a similar but slightly smaller value than that for hydrogen reduction (3.304). The ratio of evaporation coefficients, $\alpha_{ev}^{(2)}/\alpha_{ev}^{(1)}$, can be evaluated from the fitting results provided that the constant C in eq 4 is the same for the two reduction conditions. In this case, this is not the real situation because the constant C contains a surface area term ($A_s$) that may vary with evaporation of ZnO powder at high temperature. However, we consider that the relevant error would be insignificant because the temperature regions corresponding to high evaporation loss were excluded during the fitting of data. Thus, the ratio $\alpha_{ev}^{(2)}/\alpha_{ev}^{(1)}$ was roughly found to be $\approx 1.5$. This indicates that evaporation of oxygen using hydrogen gas is an easier process than that with activated carbon. It seems that the smaller hydrogen molecules are able to react with oxygen atoms located at geometrically unfavorable sites.

For example, surface atoms in a completed crystal plane will have more bonding with neighboring atoms than those located at kink or ledge sites, which makes it difficult for the atoms to evaporate. The difference between the average number of bonds that break in the two reduction processes may be explained analogously: because hydrogen molecules can produce oxygen vacancies at less exposed and more highly bonded sites, the evaporation coefficient, which is a measure of the kinetic efficiency, is larger than that for the CO case, and the average number of bonds that break to form an oxygen vacancy is also higher (although the difference is slight).

As mentioned above, the similar Gibbs free energies calculated for the two cases indicate that eqs 1 and 2 are suitable as models for the formation of oxygen vacancies. There may be some discrepancy from the actual formation energy due to measurement errors and the reduction process not being maintained at equilibrium. Careful adjustment of influential factors such as the evaporation of zinc, air leakage, and reactions during the heating and cooling processes is expected to improve the measurement accuracy.

5. Conclusions

The formation reaction of an oxygen vacancy in ZnO, which is expressed as $\text{O}_\text{ZnO} \rightarrow \nu \text{ZnO} \rightarrow \nu \text{Zn} + \nu O$, was analyzed using a thermodynamic approach. The enthalpy and Gibbs free energy at 298 K were determined. For hydrogen reduction, these values were calculated to be 6.06 and 5.44 eV, respectively; for activated carbon, they were calculated to be 5.90 and 5.36 eV, respectively. The use of the PL green emission intensity as a measure of vacancy concentration allowed experimental data to be used in calculations. The evaporation coefficient and average energy of bonds broken during the formation of an oxygen vacancy were larger for hydrogen reduction than for CO reduction; this is considered to be due to hydrogen molecules being able to react better with oxygen atoms in geometrically unfavorable locations.

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Supporting Information Available: PL emission spectra of ZnO reduced in a pure nitrogen atmosphere and reported values of formation energy of oxygen vacancy, which are calculated on the basis of first principles methods. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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