Oxygen vacancies: the origin of n-type conductivity in ZnO

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Oxygen vacancy (V₀) is a common native point defects that plays crucial roles in determining the physical and chemical properties of metal oxides such as ZnO. However, fundamental understanding of V₀ is still very sparse. Specifically, whether V₀ is mainly responsible for the n-type conductivity in ZnO has been still unsettled in the past fifty years. Here we report on a study of oxygen self-diffusion by conceiving and growing oxygen-isotope ZnO heterostructures with delicately-controlled chemical potential and Fermi level. The diffusion process is found to be predominantly mediated by V₀. We further demonstrate that, in contrast to the general belief of their neutral attribute, the oxygen vacancies in ZnO are actually +2 charged and thus responsible for the unintentional n-type conductivity as well as the non-stoichiometry of ZnO. The methodology can be extended to study oxygen-related point defects and their energetics in other technologically important oxide materials.

Among metal oxides, ZnO is a prototypical n-type material with numerous applications, including catalysts, gas sensors, varistors and transparent electrodes etc. Renewed interest has recently emerged for its ultraviolet light emission capabilities¹. Progress towards ZnO-based optoelectronic devices and applications, however, has been impeded largely by unintentional and seemingly unavoidable n-type conductivity of ZnO materials that makes stable p-type doping extremely daunting. In order to solve this most puzzling problem for ZnO, it is highly desirable to understand the origin of the unintentional n-type conductivity²–⁶.

It is generally accepted that the oxygen vacancy (V₀) plays a central role in determining the physical and chemical properties of metal oxides; it dominates various diffusion mechanisms involved in doping and its limitation, processing and device degradation, minority carrier lifetime, and luminescence efficiency etc.⁷–¹³. Specifically, V₀-related issues are of particular interest for ZnO. Whether the above-mentioned n-type conductivity comes from V₀ has remained as a major problem in ZnO for a long time: O-deficient ZnO easily behaves as an n-type semiconductor even without the introduction of any intentional dopants¹⁴. Theoretical studies¹⁵–¹⁷ seem consistently to indicate that V₀ has the lowest formation enthalpy among the donor-like point defects. However, it leads to a deep electronic state in ZnO so that V₀ could not be ionized and contribute to the conductivity at room temperature. The theoretically derived V₀ defect energetics exhibits huge controversy probably owing to the finite-supercell formalism and the inaccurate description of the band structure of ZnO¹⁸; the formation enthalpy ΔHᵋ of neutral V₀ under O-poor conditions ranges from -0.8 to 3.9 eV¹⁵–¹⁷. A formation enthalpy ΔH ≥ 3.9 eV as reported in Ref. 15 implies a V₀ concentration C(V₀) < 10⁸ cm⁻³, which is far below the experimental value of 10¹⁷–10¹⁹ cm⁻³¹⁹–²¹. In the experimental side, most proposed models rely on some circumstantial methods and evidences¹⁴,²². Moreover, the charge state of V₀ is much less addressed and remains as a controversial issue in ZnO.

To resolve these problems, we conduct a systematic study of oxygen self-diffusion in ZnO. Our study employs a unique oxygen-isotope ZnO heterostructures with delicately-controlled chemical potential (μ) and Fermi level (Eᵋ). Unlike the gaseous-exchange technique, which has absorption and evaporation problems²³,²⁴, the self-diffusion in the isotope heterostructures provides reliable information on the energetics and electronic properties of point defects²⁵–²⁷.
show unambiguously that the diffusion process of oxygen atoms in ZnO is predominantly mediated by V$_{O}$ rather than oxygen interstitial (O$_i$). We further demonstrate that the oxygen vacancies in ZnO are $+2$ charged even near the conduction band minimum, in contrast to the general belief of their neutral attribute. The results establish that the oxygen vacancies are the dominant donor-like native point defects and thus responsible for the unintentional n-type conductivity as well as the non-stoichiometry of ZnO.

It is well known that defect formation process is closely associated with defect formation process. The defect formation enthalpy $\Delta H_f$ is given by

$$\Delta H_f(D^i, \mu, E_F) = E(D^i) - E_F + \mu + q(E_F + E_{VB}) \quad (1)$$

where $E(D^i)$ is the total energy of the semiconductor with defect D in a charge state of q, and $E_F$ is the energy of the perfect host. $\mu$, $E_F$ and $E_{VB}$ are the atomic chemical potential, the Fermi level and the valence band maximum, respectively. Thus, the value of q, i.e., the charge state of a specific defect $D^i$, can be deduced from the dependence of $\Delta H_f$ on $E_F$.

![Figure 1](image)

Figure 1 | $^{18}$O concentration depth profiles in as-grown samples. Samples labeled as Z1 to Z5 were grown with decreased Zn/O ratio. The inset shows the schematic structure of these samples.

To confirm the role of V$_{O}$ in the n-type conductivity, the first thing is to determine whether and to what extent it is involved in the diffusion in the heterostructures. As can be seen from Eq. (1), $\Delta H_f$ is linearly related to $\mu$,$^{28}$ and will increase and decrease in V$_{O}$- and O$_i$-dominated diffusion processes, respectively, when $\mu$ moves towards O-rich conditions and the influence of $E_F$ and other factors is negligible. A series of heterostructures consisting of top $^{18}$O-enriched Zn$^{18}$O and bottom natural Zn$^{9}$O layers on sapphire were thus synthesized with different chemical potentials and same Fermi levels, labeled as Z1, Z2, Z3, Z4 and Z5, respectively, as schematically illustrated in the inset of Fig. 1(a).

The modulation of chemical potentials was realized through a gradually decreased Zn flux under a constant O flux. According to the growth rate, Z1 and Z2 can be regarded as Zn-rich samples while Z3 – Z5 O-rich ones$^{29}$ (Supplementary Information Fig. S1). The curves in Fig. 1 show the $^{18}$O concentration depth profiles for the as-grown samples. The enriched Zn$^{18}$O layers are immediately evident by the higher concentration of $^{18}$O with respect to that in the bottom Zn$^{9}$O layers. Interestingly, the $^{18}$O profiles obviously become steeper when the $\mu$ moves towards O-rich conditions.

According to the Fick’s law, the self-diffusion profile of $^{18}$O across an interface is described by$^{27}$

$$C(x) = \frac{C_1 + C_2}{2} - \frac{C_1 - C_2}{2} \text{erf}\left(\frac{x}{2\sqrt{Dt} + k}\right), \quad (2)$$

where $x = 0$ is at the interface, $C_1$ and $C_2$ are the initial $^{18}$O concentrations at the top and bottom sides of heterostructures, respectively, and erf(x) is the error function. The characteristic diffusion length is $l \quad (l = 2\sqrt{Dt})$, where $D$ is the self-diffusion coefficient (i.e., diffusivity) and $t$ is the annealing time. A correction factor $k$ is introduced in the fitting procedure owing to the initial distribution. The O self-diffusion coefficient $D$ can be therefore derived based on Eq. (2). Figure 2(a) shows the typical $^{18}$O concentration depth profiles of Z5 and their fitting curves as a function of annealing temperature using Eq. (2). The diffusion of $^{18}$O atoms becomes more pronounced at elevated annealing temperature. As illustrated in Fig. 2(b), the samples with gradually varied chemical potentials show different profiles after annealing at 1073 K for 30 min. Note that $D$ has a negatively exponential relation to the activation enthalpy $\Delta H_a$, i.e., $D = D_0 \exp(-\Delta H_a/k_BT)$ , where $D_0$, $k_B$ and T denote the pre-exponential factor, Boltzmann constant and temperature, respectively. Thus, using the data of $D$ at different temperatures, the activation enthalpies $\Delta H_a$ can be obtained. Arrenhius plots of all of the
extracted $D$ values versus the corresponding reciprocal absolute temperatures are presented in Fig. 3. As shown in Fig. 3, $\Delta H_a$ is 1.10 ± 0.04 eV, 1.32 ± 0.05 eV, 1.53 ± 0.04 eV, 1.69 ± 0.03 eV and 2.56 ± 0.06 eV for Z1-Z5, respectively, when $\mu$ moves towards O-rich conditions.

It is well established that $D$ is temperature-dependent and affected by (i) the chemical potential $\mu$ (i.e., the partial pressures of Zn and O), (ii) the Fermi level $E_F$, and (iii) intentional or unintentional doping, i.e., externally controlled mechanism. To determine the dominant diffusion path in Z1-Z5, the influence of $E_F$ and dopants on $D$ has to be excluded first. In this case, $D$ (and hence $\Delta H_a$) will be more predominantly controlled by $\mu$.

In our case, the carrier concentrations of Z1 to Z5 were obtained by temperature-dependent Hall measurements in vacuum from 473 K – 823 K, and reached a nearly identical value, resulting in an almost constant $E_F$ value in the range of 673 K – 823 K (Supplementary information Fig. S2). Note that $E_F$ is estimated based on the well-known formula $E_F = E'_F + k_B T \ln(n_e/n_i)$, where $E'_F$, $n_e$ and $n_i$ denote Fermi level under the intrinsic condition, the carrier concentration and the intrinsic carrier concentration, respectively. The temperature dependence of the band gap $E_g$ is also taken into account in the above case. The plots of $E_F$ versus T are then reasonably extrapolated to the annealing temperature region in the diffusion experiments. As a result, an almost fixed $E_F$ is obtained for the five samples Z1 to Z5, suggesting that the influence of $E_F$ on the diffusion coefficient $D$ can be neglected.

Further, the defect concentrations can also be externally controlled, e.g., through intentional or
unintentional doping. If impurity concentration is high enough, the dependence of $D$ and $\Delta H_a$ on $\mu$ should be significantly less pronounced. However, for our samples, the diffusivity $D$ increases by more than one order of magnitude when varying $\mu$ at 1023 K, as illustrated in Fig. 3. Moreover, the concentration of those unintentionally-doped impurities is relatively low (Supplementary information Fig. S3) so that their effect on $D$ is negligible. As a result, the diffusivity $D$ of the isotopic heterostructures - Z1 to Z5 - is primarily controlled by $\mu$, which is the first goal of our experimental designs. Indeed, $\mu$ can control the defect concentrations and thus influence the diffusion process (Supplementary Information).

Under the assumption that the diffusion is a conventional point-defect-mediated process, the activation enthalpy $\Delta H_a$ of the diffusion defect species can be considered as the sum of the formation enthalpy $\Delta H_f$ and the migration enthalpy $\Delta H_m$. The relatively low $\Delta H_a$ (1.10 ± 0.04 eV) for Z1 suggests that a direct diffusion mechanism without the need of forming thermally-activated defects is more reasonable, namely the diffusing atoms simply jump into neighboring vacancy sites. Consequently, the activation enthalpy for Z1 is essentially determined by the migration enthalpy. For Z2 to Z5, on the other hand, the increased $\Delta H_a$ and lower $D$ values at identical temperatures shown in Fig. 3 indicate that the defects of mediating diffusion are less favorable under O-rich conditions. In the case that only $V_O$ and $O_i$ are involved in diffusion, $V_O$ should dominate the above-mentioned self-diffusion process. Otherwise, if $O_i$ is dominant, the trend for $\Delta H_a$ and $D$ from Z1 to Z5 would be opposite. Moreover, it is consistent with the monovacancy model, in which the migration enthalpy of vacancy $\Delta H_m^v$ is described by$^{31,32}$

$$\Gamma_o = \sqrt{\frac{8\Delta H_m^v}{3m\lambda}},$$

where $\Gamma_o$, $m$ and $\lambda$ represent the frequency of the highest vibrational mode in the crystal, the mass of O atom and the lattice constant, respectively. Taking $\Gamma_o = 8 \times 10^{12}$ Hz$^{27,33}$ and $\lambda = 0.52$ nm$^{34}$ into account, we obtain $\Delta H_m^v = 1.08$ eV, which is in a good agreement with $\Delta H_a = 1.10 \pm 0.04$ eV for Z1 sample (Fig. 3).

To figure out the dependence of $\Delta H_f$ on $E_F$ and the charge state q of $V_O$, we investigate the influence of $E_F$ on O diffusion. The modulation of $E_F$ was achieved by effective Ga doping. Two more series of samples were studied. The first batch of samples Z1-1 and Z1-2 were grown using the conditions identical to those for Z1, except for in-situ Ga doping contents of $\sim 2.0 \times 10^{18}$ cm$^{-3}$ and $\sim 6.0 \times 10^{18}$ cm$^{-3}$, respectively (Supplementary information Fig. S4). The
second batch of samples Z2-1 and Z2-2 has Ga concentrations of ~3.0×10^{18} cm^{-3} and ~1.5×10^{19} cm^{-3}, respectively (Supplementary information Fig. S5). As illustrated in Fig. 4(a), the diffusion process is significantly retarded in Ga-doped samples. According to the Arrhenius plots in Fig. 4(b), the activation enthalpy ΔH_a increases from 1.10 ± 0.04 eV for the undoped sample Z1 to 1.56 ± 0.07 eV for the Ga doped Z1-2. The ΔH_a for Z2, Z2-1 and Z2-2 shows similar behavior and increases from 1.32 ± 0.05 eV for Z2 to 1.77 ± 0.02 eV for Z2-2 (Supplementary information Fig. S6). After annealing (up to 1123 K) the secondary ion mass spectroscopy (SIMS) measurements do not reveal a significant redistribution of Ga compared to the as-grown samples (Supplementary information Fig. S7), indicating that Ga dopant diffusion is negligible. Since the Zn/O ratio and thus μ are fixed for each batch of samples, the change in ΔH_a should be mainly attributed to the Fermi level change after Ga doping. Indeed, the Fermi level is below the conduction band minimum by 0.35 eV, 0.18 eV and 0.12 eV\(^{30}\) for undoped Z1 and Ga-doped Z1-1 and Z1-2 with carrier concentration of 1.0×10^{17} cm^{-3}, 1.0×10^{18} cm^{-3} and 2.3×10^{18} cm^{-3}, respectively, at 823 K.

The result of the increased activation enthalpy with the upward Fermi level indicates that Vo is charged, which constitutes another finding of our study. Since ΔH_f of charged defects is linearly related to E_F and ΔH_m is independent on E_F and μ for defects with a given state, ΔH_m is linearly dependent on E_F for defects with a given state. Accordingly, the slope of ΔH_a - E_F curve gives the charge number q of the defects. The results for Z1 to Z1-2 and Z2 to Z2-2 are shown in Fig. 5. We can clearly see that ΔH_a increases with E_F, which is in contrast to the theory horizontal lines\(^{15}\). The fitting for both batches of samples gives a consistent value of q_1, q_2 = +1.8, indicating that the dominant VO is +2 charged even near the conduction band minimum. The ionized VO is a shallow donor and thus gives rise to the n-type conductivity in ZnO. The obtained ΔH_m = 1.10 eV therefore corresponds to the migration barrier for +2 charged VO, which is excellent agreement with the theoretical result – 1.09 eV\(^{33}\).

In conclusion, we have investigated the self-diffusion process of oxygen atoms as a function of μ and E_F in oxygen-isotopic ZnO heterostructures. It is found that VO dominates the diffusion process with an activation enthalpy of 1.10 eV – 2.56 eV from Zn-rich to O-rich growth conditions. We have deduced the migration enthalpy to be 1.10 eV and found that the formation enthalpy of VO increases even when E_F moves towards the conduction band minimum. Our results reveal that VO is +2 charged even near the conduction band minimum, which is opposite to the usually believed neutral state. Our study establishes oxygen vacancies as the dominant donor-like native point defects in ZnO and well explains the unintentional n-type conductivity, a mysterious problem in the last fifty-year study of ZnO. The methodology we have developed can be used to study oxygen-related point defects and their energetics in other technologically important metal oxides such as TiO_2 and In_2O_3, and thus is of general interest in oxide and semiconductor physics community.

**Methods**

Isotopically modulated samples were grown by radio-frequency plasma assisted molecular beam epitaxy (rf-MBE) on c-oriented sapphire substrate with several-nanometer-thick nitrided structure on the
surface, and more nitridation pretreatment details can be found elsewhere. The base pressure was in the range of 10⁻⁹ mbar. Two sorts of oxygen sources were used in the synthesis, one in its natural isotopic ratio (labeled as ¹⁸O) and another one artificially enriched with ¹⁶O isotope (> 99.7%). A ZnO buffer layer was firstly deposited at 723 K, providing a good epitaxial template. Further, a ZnO₇ epitaxial layer and an ¹⁸O-enriched ZnO layer were subsequently grown at 873 K. To realize the study of diffusion profiles as a function of \( \mu \), the Zn flux was varied for different samples, while the radio frequency power of the plasma gun and the flux of oxygen gas were kept constant – 300 W and 2.0 standard cubic centimeter (sccm), respectively. Specifically, the temperature of Zn K-cell for Z1 – Z5 is 605 K, 591 K, 585 K, 579 K and 569 K, respectively. Thus, a series of isotopic heterostructures consisting of top Zn¹⁸O and bottom Zn⁶O were synthesized. It should be noted that the ¹⁸O source used in the top Zn¹⁸O layer was mixed with 1.0 sccm artificially enriched ¹⁸O (> 99.7%) and 1.0 sccm ¹⁶O, and the chemical potentials of Zn and O were respectively kept the same for the two different epilayers in each sample. Reflection high-energy electron diffraction (RHEED) was utilized in-situ to monitor the whole epitaxial growth processes (Supplementary information Fig. S8).

Prior to the diffusion anneal, the surfaces of two identical samples were brought together in a diffusion couple to minimize the evaporation. Annealing experiments were performed in a temperature range of 1023 K – 1148 K for 30 min in vacuum. In order to ensure a fast ramping up to the desired diffusion temperature, the removable furnace was preheated and then moved to the sample place to perform the annealing process. The annealing temperatures were controlled within ± 2 K. After annealing, the furnace was moved away immediately. Note that the annealing temperature range is 1023 K – 1173 K for the two more batches of samples with modulated Fermi level – Z1 to Z1-2 and Z2 to Z2-2.

Concentration depth profiles were measured by secondary ion mass spectroscopy (SIMS) using a Hitachi MAXIM Analyser. For SIMS analysis 5 keV Ar⁺ ions with a current 220 nA was used as a primary beam raster over an area of 200x200 µm². The signal-to-concentration calibration was performed using standard ¹⁶O and ¹⁸O samples as reference. The conversion of SIMS sputtering time to depth profiles was performed by measuring the crater depth using a Dektak 8 profilometer and assuming a constant erosion rate. Temperature-dependent Hall measurements were performed by HL5500PC Hall Effect Measurement System.

Note that the error bars in Fig. 3 - 5 can be explained by the inaccuracy originated from the uncertainty in SIMS measurements. The fact that SIMS sputtering rate is not being constant will lead to a maximum error of 20% in \( D \). The analysis of \( D_0 \) and \( \Delta H_e \) indicates that the values are within the acceptable limit and supports our above discussions (Supplementary Information S9).

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**Author Contributions**

Z.M., Q.X. and X.D. conceived and guided the study. L.L. and Z.M. designed the research. L.L. and Q.X. conducted the growth and characterization. L.L., Z.M., X.D. A.A. A.K. and Q.X. did the analysis. All authors discussed the results and commented to the manuscript.

**Additional Information**

Supplementary information is available from Online or from the author.

**Competing financial interests**

The authors declare no competing financial interests.