# Anionic and Hidden Hydrogen in ZnO

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# Anionic and "Hidden" Hydrogen in ZnO

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First-principles calculations are performed to study energetics and kinetics of hydrogen in ZnO, in particular, the $H^-$ anion and the $H_2$ molecule on the interstitial site and in the oxygen vacancy. We show that the $H_2$ molecule kinetically trapped in the oxygen vacancy, rather than interstitial $H_2$, can explain a variety of experimental observations on "hidden" hydrogen in ZnO. The accumulation of shallow donors, especially the substitutional H, near ZnO surface is important to the formation of "hidden" hydrogen in ZnO bulk and can also lead to persistent photoconductivity.

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ZnO is a promising wide-gap semiconductor for blue/UV optoelectronics[1] and is also a fast scintillator that may be used for radiation detection.[2] Hydrogen in ZnO has been extensively studied in the last ten years[3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15] because unintentionally doped H is usually found in ZnO, including many commercial ZnO samples.[6] Interstitial and substitutional H have been shown by first-principles calculations to be shallow donors (i.e., $H_i^+$ and $H_O^+$), which contribute to the *n*-type conductivity in ZnO.[3, 12] Subsequent experiments confirmed that hydrogen incorporation increases the electron carrier density in ZnO.[6] The O-H vibrational frequencies have also been observed by IR spectroscopy.[4, 5, 8, 9]

Annealing experiments have been performed to understand the thermodynamics and kinetics of H in ZnO. High temperature (750 °C-1000 °C) annealing of ZnO in the $H_2$ environment incorporates a large amount of $H_i$ and $H_O$ ($10^{17} – 10^{18}$ $cm^{-3}$) in ZnO.[6, 13, 14] Subsequent quenching and annealing at lower temperatures removes atomic hydrogen from ZnO. $H_i$ can be annealed out of ZnO at 150 °C while $H_O$ is eliminated between 500 °C to 700 °C.[6] It appears that a "hidden" hydrogen reservoir exists in ZnO and can release $H_i$ when the temperature is > 400 °C.[6] The "hidden" hydrogen species are invisible by the IR spectroscopy. The interstitial $H_2$ molecule ($H_{2,int}$) was suggested to be a candidate for the "hidden" hydrogen.[6] Recently, $H_2$ molecules have indeed been identified by a Raman study when ZnO is annealed without external hydrogen at 550 °C following annealing at 1000 °C in an $H_2$ environment.[14]

Despite this progress, we find that the H behavior is nontrivial and far from being understood. In particular, if assuming the "hidden" hydrogen is $H_{2,int}$, the H behavior cannot be reconciled with basic thermodynamic principles. First of all, the basic question

that needs to be answered is whether $H_i^+$ or $H_{2,int}$ is the more stable hydrogen species in ZnO. Obviously, this depends on the hydrogen chemical potential and Fermi level. The higher the H chemical potential, the more likely the diatomic species like $H_2$ would be more stable. Also, since $H_i^+$ is a donor while $H_{2,int}$ is neutral, the $[H_i^+]/[H_{2,int}]$ ratio should increase with decreasing Fermi level. High-temperature annealing under $H_2$ environment provides a condition that is close to the thermal equilibrium for H in ZnO. Under this condition, $H_i^+$ is found to be abundant while no $H_2$ is found,[14] which suggests that $H_i^+$ is more stable than $H_2$. However, with subsequent annealing at lower temperatures without external H (lower H chemical potential), $H_i^+$ disappears (which results in lower Fermi level) while $H_2$ appears.[14] It is thus puzzling that a lower H chemical potential and a lower Fermi level promote the formation of $H_{2,int}$ at the expense of $H_i^+$. These conflicting results for hydrogen in ZnO warrant a re-examination of the hydrogen energetics and kinetics in ZnO.

Besides the above puzzling experimental results, there are also unanswered fundamental questions on H chemistry in ZnO. H in ZnO has been predicted by theory and confirmed experimentally to be a shallow donor, rather than an amphoteric impurity,[3, 6] meaning that the H (+/-) level is above the conduction band minimum (CBM). However, the $H_i^-$ structure has never been identified. The $H_i^-$ ion discussed in the literature, i.e. bond-center (BC) or anti-bonding (AB) $H_i^-$ coordinated with one oxygen atom, is actually an $H_i^+$ with two free electrons.[3] Thus, from theoretical point of view, the proof of $H_i$ as a shallow donor in ZnO is not complete until we find both $H_i^+$ and $H_i^-$ structures and calculate the (+/-) transition level. The knowledge of chemistry of

anionic hydrogen is important to the understanding of hydrogen chemistry in ZnO and in semiconducting and ionic materials in general.

We have carried out a comprehensive study of the interactions of atomic hydrogen (including both $H_i^+$ and $H_i^-$ ions) and $H_2$ molecules with the ZnO lattice and the low-energy oxygen vacancy ($V_O$). We show that the (+/-) transition level for $H_i$ is located at 0.34 eV above CBM. We also suggest that the $H_2$ local vibrational modes (LVMs) observed by Raman spectroscopy may originate from an $H_2$ molecule trapped in an oxygen vacancy ($V_O^{2+}$-$H_2$) rather than from $H_{2,int}$. As a result of the $H_O^+$ accumulation near the surface, $V_O^{2+}$-$H_2$ should exist in the interior of the ZnO sample where the Fermi level is lower and also the persistent photoconductivity may occur due to the surface band bending.

Our calculations are based on the plane-wave projector augmented wave method[16] with Heyd-Scuseria-Ernzerhof (HSE) hybrid functional.[17, 18] unless otherwise noted, as implemented in the vasp code.[19, 20] The screening parameter of the non-local Fock exchange is set at 0.2 $Å^{-1}$.[18] We use 37.5% of the non-local Fock exchange in the HSE functional to produce a band gap of 3.47 eV, which is in good agreement with the experimental value. The cutoff energy for the plane-wave basis is 400 eV. All the calculations were performed using 96-atom supercells. A 2×2×2 grid was used for the k-point sampling of the Brillouin zone. All the atoms were relaxed to minimize the Feynman-Hellmann forces to below 0.05 eV/Å. The methods for calculating formation energies and transition energy levels can be found in Ref. 21.

We will begin by discussing the interaction of $H^-$ with the ZnO lattice and the oxygen vacancy. We find that $H_i^-$ prefers to be located in the hollow hexagonal channel,

binding with three Zn atoms, as shown in Fig. 1(a), rather than on BC or AB sites as investigated in Ref. 3. Multi-coordination is often seen for ionic bonding, which is governed by Coulomb attraction and electron shell repulsion.[22] ($H_i^+$ is an exception as it has no electron shell and thus favors a single bond.) $H_i^-$ in ZnO induces a fully occupied deep gap level (H 1*s* level) at $E_v$ + 1.66 eV. However, $H_i^-$ is only metastable as shown in Fig. 2. The (+/-) transition level for $H_i$ is 0.34 eV above the CBM, explaining why $H_i$ is a shallow donor in ZnO.

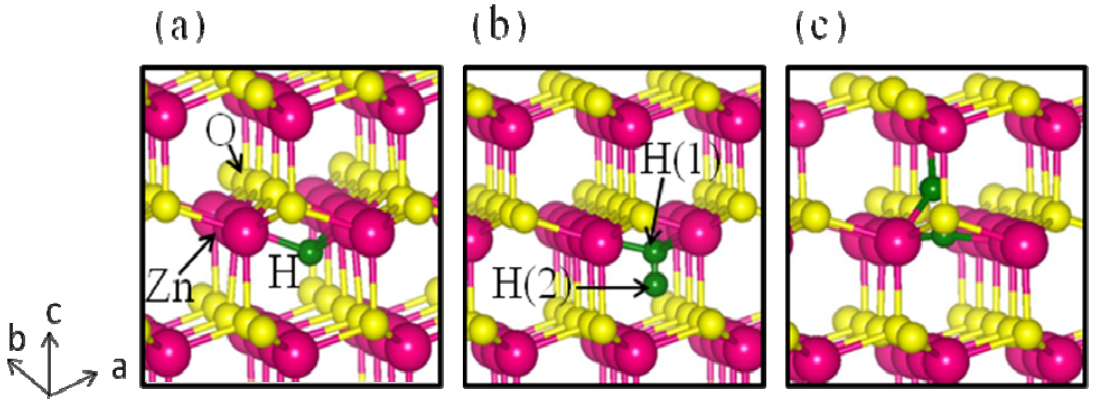


FIGURE 1. (Color online) Structures of (a) interstitial $H^-$ ion ($H_i^-$), (2) interstitial $H_2$ ($H_{2,int}$), and (3) two $H^-$ ions in an oxygen vacancy ($V_O^{2+}$-2$H^-$).

We have shown previously that $H^-$ can bind with anion vacancies in II-VI semiconductors.[22] $H^-$ may be located on or off-center in the anion vacancy, depending on the size of the anion vacancy relative to the ionic radius of $H^-$. In the case of ZnO, $H^-$ occupies the center of $V_O^{2+}$, effectively forming a substitutional $H_O^+$. Here, we find that a $V_O$ can further trap a second $H^-$ to form $V_O^{2+}$-2$H^-$, with overall charge state to be neutral. In $V_O^{2+}$-2$H^-$, each $H^-$ binds with two Zn atoms as shown in Fig. 1(c). Based on the calculated formation energy of 1.63 eV (assuming O-poor and H-rich limits), the

concentration of $V_O^{2+}$-2 $H^-$ in ZnO should range from $10^{14}$ to $10^{16}$ $cm^{-3}$ if ZnO is hydrogenated at 750-1000 °C. One should also be aware that $V_O^{2+}$-2 $H^-$ may be sensitive to light excitation since it induces a fully occupied deep level at $E_v$ + 0.77 eV and it is known that $H^-$ in the anion vacancy of alkali halides is a color center ($U$ center).[23, 24, 25] Removing one or two electrons from the deep gap level of $V_O^{2+}$-2 $H^-$ will change the distance between the two H atoms from 2.10 to 1.07 or 0.75 Å. With two electrons removed, the H-induced level will be cleared from the band gap and the two $H^-$ ions become an $H_2$ molecule. The occupied deep level by $V_O^{2+}$-2 $H^-$ can be viewed as the filled anti-bonding orbital of an $H_2$ molecule.

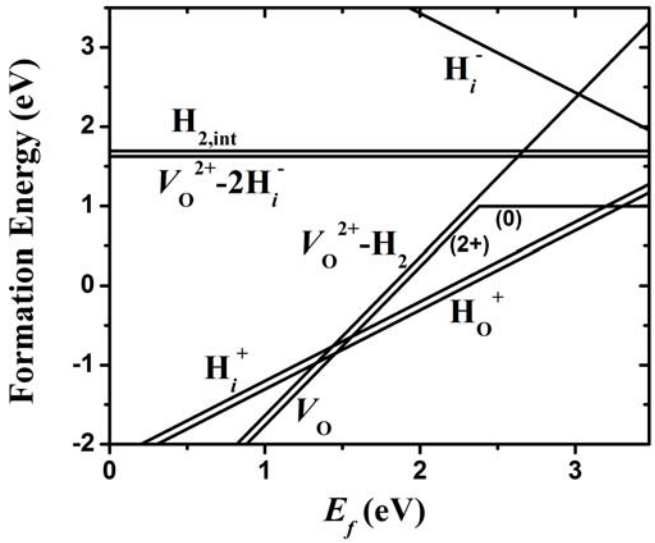


FIGURE 2. Formation energies of hydrogen and oxygen vacancy related defects in ZnO. The slope of the energy lines indicates the charge state of the defect, as selectively shown. The point, at which the slope changes, is the transition energy level.

The calculated Zn-H stretching modes for $V_O^{2+}$-2 $H^-$ are 1875 ($\perp c$ axis) and 1692 ($\| c$ axis) $cm^{-1}$, respectively. These LVMs have not been observed. However, based on

the calculated formation energy and defect concentration, these LVMs may be observable by IR spectroscopy provided that ZnO is hydrogenated at high temperature (>1000 °C) and that the light excitation of the $H^-$-induced deep level is avoided.

Our calculations show that $H_i^+$ is more stable than $H_{2,int}$ in the entire range of accessible Fermi energy (see Fig. 2). This is consistent with the experimental observation of $H_i^+$ but not $H_2$ after hydrogenation at high temperature (>1000 °C), [14] which provides a condition close to the thermal equilibrium for H in ZnO. The results shown in Fig. 2 assume an H-rich condition. One should note that reducing the H chemical potential will increase the formation energy of $H_{2,int}$ faster than that of $H_i^+$. Surprisingly, the LVMs of $H_2$ is observed by Raman spectroscopy while $H_i^+$ is annealed out at lower temperature (550 °C) without external H (lower H chemical potential). These results suggest that the $H_2$ molecules that are observed by Raman spectroscopy may not be $H_{2,int}$.

The interstitial $H_2$ is aligned along the *c* axis in the hollow hexagonal channel in ZnO.[3,10] As may be seen from Figs. 1(a) and (b), one of the H atoms in $H_{2,int}$ occupies a position close to the $H_i^-$ site. The Zn-H bond lengths are 1.85 and 1.98 Å for $H_i^-$ and $H_{2,int}$, respectively. It is, therefore, conceivable that $H_{2,int}$ is slightly polarized with the H(1) in Fig. 1(b) slightly negatively charged whereas the H(2) is slightly positively charged. The calculated LVMs for $H_{2,int}$ and $D_{2,int}$ are 4460 and 3154 $cm^{-1}$, respectively. When both H and D are present, the LVMs for $HD_{int}$ are either 3875 or 3861 $cm^{-1}$, depending on whether D occupies the H(1) or H(2) site. The splitting of the H-D stretching modes by 14 $cm^{-1}$ is not insignificant, reflecting the fact that the H(1) and H(2) sites are not equivalent as a result of Zn-H(1) bonding. However, the polarization of $H_{2,int}$

is small and it should therefore still be Raman active. Raman spectroscopy with resolution <5 $cm^{-1}$ did not find such H-D mode splitting.[14] This further casts doubt on whether the observed $H_2$ LVMs indeed result from $H_{2,int}$.

Here we propose that the "hidden" hydrogen in ZnO is the $H_2$ molecule trapped in the oxygen vacancy ($V_O^{2+}$-$H_2$). The $H_2$ in $V_O^{2+}$ is surrounded by four Zn atoms that are located at the vertices of an approximate tetrahedron. As a result, the $H_2$ in $V_O^{2+}$ has nearly no polarization, in contrast to $H_{2,int}$, and is nearly a free rotator as also suggested experimentally.[14] The calculated $H_2$, $D_2$, and HD LVMs are in excellent agreement with experimental results, as shown in Table I. In particular, the H-D LVM splitting is negligible, consistent with the experiments.

Table I. Local vibrational frequencies (LVMs) of calculated and measured $H_2$, $D_2$, and HD in the interstitial site and oxygen vacancy of ZnO. The LVMs of the free $H_2$ molecule are also shown. The units are in $cm^{-1}$.

| | $H_{2,int}$ | $D_{2,int}$ | $HD_{int}$ | $V_O^{2+}$ - $H_2$ | $V_O^{2+}$ - $D_2$ | $V_O^{2+}$-HD | Free $H_2$ |
|---|---|---|---|---|---|---|---|
| Theory | 4460 | 3154 | 3875<br>3861 | 4277 | 3025 | 3705<br>3703 | 4448 |
| Exp. | | | | 4145† | 2985† | 3628† | 4395‡ |

† Ref. 14; ‡ Ref. 26

ZnO is typically *n*-type with the Fermi level near CBM. Under this condition, $H_{2,int}$ should be more stable than $V_O^{2+}$-$H_2$ as shown in Fig. 2. However, the interior of the ZnO sample can be much more insulating, favoring the formation of $V_O^{2+}$-$H_2$. The "hidden" hydrogen was suggested to form in the temperature range of 150 - 450 °C, in which $H_i^+$ is annealed out while $H_O^+$ remains.[6] The $H_2$ LVMs were observed by Raman spectroscopy in a much larger-sized ZnO sample annealed at 550 °C for 30 minutes.[14]

The annealing was sufficient to eliminate all $H_i^+$ but the annealing time was too short to anneal out all $H_O^+$,[27] which has a much higher diffusion barrier than $H_i^+$.[11, 12] In both cases, the majority of the H donor, i.e., $H_i^+$, is eliminated.[28] As a result, the carrier density is substantially lowered. The remaining dominant donor, $H_O^+$, is heavily concentrated near the ZnO surface because the oxygen vacancies are mostly created near the surface during high-temperature annealing.[13, 15] The $H_O^+$ penetration depth is shown to be 5-6 μm when ZnO undergoes H annealing at 750 °C.[15] Zn interstitials ($Zn_i$), which are highly mobile native donors,[29, 30, 31] are also likely to accumulate near the surface because the extra $Zn_i$ resulted from quenching of ZnO from high temperature (as was done in Ref. 6 and 14) may tend to phase-separate to the surface. As a result, the surface band bending occurs, creating a depletion layer extending from the surface to the interior of the ZnO sample. The interior of the ZnO sample should have much lower carrier density and Fermi level. As shown in Fig. 2, the lower Fermi level promotes the formation of $V_O^{2+}$ and hence $V_O^{2+}$-$H_2$. Meanwhile, the non-equilibrium factor also plays a role in ionizing $V_O^0$. The oxygen vacancy in ZnO is a color center in ambient environment,[32] indicating strong light absorption by $V_O^0$ leading to the formation of $V_O^{2+}$. The photo-ionization of $V_O^0$ has been suggested to contribute strongly to the *n*-type conductivity in ZnO.[33] Therefore, the combination of low carrier density in bulk and the high light absorption at $V_O^0$ may lead to the formation of $V_O^{2+}$-$H_2$ in bulk ZnO. Indeed, it was found that Raman spectroscopy of $H_2$ LVMs is sensitive to the excitation spot in the ZnO sample,[27] and that $H_2$ and $H_O^+$ in ZnO anti-correlate,[14] which means that $H_2$ is not distributed near the

surface. Our $V_O^{2+}$-$H_2$ model predicts that $H_2$ should be located in the bulk near the boundary of the surface depletion region. However, there is no mechanism to justify the anti-correlation between $H_{2,int}$ and $H_O^+$.

During the high temperature hydrogenation, the carrier density is very high in bulk ZnO due to the existence of large amount of fast-diffusing $H_i^+$ (Ref. 7 and 11). Such environment favors $V_O^0$ over $V_O^{2+}$ and consequently suppresses the formation of $H_2@V_O^{2+}$. This explains why $H_2$ LVMs are not detected in high-temperature hydrogenated ZnO.[14]

$V_O^{2+}$-$H_2$ is a metastable species. It is unstable against the following reaction, $V_O^{2+}$-$H_2 \rightarrow H_i^+ + H_O^+$, which lowers the energy by 0.87 eV. $H_i^+$ is unstable when T > 150 °C. Therefore, the observation of $H_2$ LVMs at 550 °C should be due to the kinetic trapping of $H_2$ by $V_O^{2+}$. The trapping energy is calculated to be 1.57 eV. In comparison, the diffusion barrier of $H_{2,int}$ is calculated to be 0.9 eV along the *c* axis and 0.6 eV on the *a*-*b* plane using Perdew-Burke-Ernzerhof exchange correlation functionals.[34] We believe that the experimental condition, in which $H_2$ LVMs were detected by Raman spectroscopy,[14] is a non-equilibrium condition. Both $H_O^+$ and $H_2$ should be in the process of out diffusion at 550 °C. We suspect that the Raman signal of $H_2$ LVMs will not survive after prolonged annealing. The weak Raman signal of $H_2$ LVMs and the sensitivity of the Raman signal to the excitation spot[14] suggest low density and inhomogeneous distribution of $H_2$ in ZnO. The detection of $V_O^{2+}$-$H_2$ requires an optimal annealing temperature and annealing time. If the annealing temperature is too high, no $H_2$ can survive. If it is too low, there would be too many $H_O^+$ in ZnO, which not only competes with $H_2$ for O vacancy sites but

also supplies electron carriers that suppress the formation of $V_O^{2+}$ in favor of $V_O^0$. Another prerequisite for $V_O^{2+}$-$H_2$ formation in ZnO is high-temperature hydrogenation, which creates oxygen vacancies. According to our best knowledge, there has not been a report on "hidden" hydrogen or on the detection of $H_2$ LVMs in ZnO treated by low-temperature H plasma, which can also introduce H into ZnO but does not create large quantity of oxygen vacancies.

Finally, we note that the good thermal stability of $H_O^+$ allows it to exist in ZnO (including many commercial samples)[9, 13] unless ZnO is annealed at high temperature (>500 °C) for sufficiently long time. This should result in surface band bending, which further has the effect of rapid separation of photo-generated electrons and holes, leading to persistent photoconductivity.

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[28] The experimental results suggest higher $[H_i^+]$ than $[H_O^+]$ (Ref. 9). On the other hand, Fig. 2 shows that the calculated formation energies of $H_i^+$ is slightly higher than that of $H_O^+$, meaning lower $[H_i^+]$ than $[H_O^+]$. The calculations assumed thermal equilibrium and the extreme O poor growth condition, which may not reflect the real experimental condition.

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