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Magnetic resonance identification of hydrogen at zinc vacancy in ZnO

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Abstract

Hydrogen (H) at a zinc vacancy (V_{Zn}) in ZnO is identified by electron paramagnetic resonance (EPR) and electron spin echo envelope modulation (ESEEM). In ZnO irradiated by 2 MeV electrons, a doublet EPR spectrum, labelled S1, was observed. The doublet structure and the accompanied weak satellites are shown to be the allowed and forbidden lines of the hyperfine structure due to the dipolar interaction between an electron spin $S=1/2$ and a nuclear spin $I=1/2$ of ^1H located at a V_{Zn} . The involvement of a single H atom in the S1 defect is further confirmed by the observation of the nuclear Zeeman frequency of ^1H in ESEEM experiments. We show that at a V_{Zn} , H prefers making a short O-H bond with one O neighbour and is off the substitutional site, forming a low symmetry C_1 defect. In this partly H passivated V_{Zn} , the unpaired electron localizes on the p orbital of another O neighbour of V_{Zn} , and not on H.

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1. Introduction

Zinc oxide (ZnO) has long been considered as one of the most promising semiconductors for optoelectronic devices [1]. Undoped as-grown ZnO exhibits n -type conductivity and p -type doping of the material is proven to be very difficult. The lack of reproducible and low resistivity p -type material [2] is the main obstacle to applications of ZnO in electronics and optoelectronics. The difficulty in p -type doping of ZnO is believed to be due to either large acceptor activation energies of common p -type dopants, such as nitrogen (N) [3], or high n -type background doping caused by intrinsic defects [4,5] and impurities such as hydrogen (H) [6].

Hydrogen is known to be present in ZnO grown by any method. Calculations showed that the formation energy of the interstitial H^+ is low enough to allow a large concentration of H in as-grown ZnO and the H interstitials at the bond-centre lattice sites (H_{BC}) act as shallow donors [6]. This has been supported by infrared (IR) absorption studies [7]. Such H defects are predicted to have a migration barrier as low as ~ 0.5 eV and can become mobile at low temperatures [8]. Therefore, thermally stable H-related defects are expected to be trapped at other defects, such as complexes between impurities and H identified by IR spectroscopy [9-11]. Hydrogen in an O vacancy (H_{O}) has been predicted to bond equally with four nearest Zn neighbours, becoming fourfold coordinated and acting also as a shallow donor in ZnO [12], or to occur simply as an anion H^- at the anion O site [13].

Hydrogen-related shallow donors have also been identified by muon spin rotation [14] and electron paramagnetic resonance (EPR) [15]. However, due to the lack of data, their microscopic models remain unclear.

In as-grown ZnO, which often exhibits *n*-type conductivity, the Zn vacancy (V_{Zn}) can capture one or two electrons to become singly or doubly negatively charged (V_{Zn}^- or V_{Zn}^{2-}). The saturation of V_{Zn}^- and V_{Zn}^{2-} by H^+ is predicted to be highly energetically favourable [16]. In hydrogenated materials using H plasma, the concentration of H exceeds that of V_{Zn} and, therefore, $V_{\text{Zn}}H_2$ is expected to be formed. This defect was suggested to be related to the H-II IR band in ZnO [17]. In a previous EPR study, Evans and co-workers [18] suggested the D and E centres in electron irradiated ZnO to be complexes between V_{Zn} and an OH^- ion. However, with very limited data (only one spectrum measured for the magnetic field along the *c* axis and no parameters for the centre have been obtained) the involvement of H in these defects remains speculative.

In this work, using undoped ZnO irradiated by 2 MeV electrons with high electron doses to create V_{Zn} with concentrations higher than that of H and other donors present in the material, we observed the EPR signals of V_{Zn}^- [19] and a new spectrum in darkness. We will from our EPR and electron spin echo envelope modulation (ESEEM) studies identify the new spectrum to be related to a single H^+ ion trapped at an O basal dangling bond of V_{Zn}^- and present the electronic structure of this partly H passivated $V_{\text{Zn}}H$ acceptor.

2. Experiment

Samples used in this study are nominally undoped ZnO substrates from Tokyo Denpa which have the resistivity of $\sim 500\text{-}1000\ \Omega\text{cm}$. The samples were irradiated by 2 MeV electrons at room temperature to doses $\sim 2\text{-}4 \times 10^{18}\ \text{cm}^{-2}$. Continuous-wave EPR measurements were performed on a Bruker ELEXSYS E500 X-band ($\sim 9.45\ \text{GHz}$) spectrometer. Electron spin echo (ESE) detected EPR and ESEEM experiments were performed on a Bruker ELEXSYS E580 X-band ($\sim 9.75\ \text{GHz}$) spectrometer. Both setups are equipped with Oxford continuous He flow cryostats, allowing the regulation of the sample temperature in the range of 4-295 K. In photoexcitation EPR (photo-EPR) experiments, a 200-W halogen lamp or a 150-W Xe lamp and appropriate optical filters were used as excitation sources.

3. Results and discussion

After irradiation, all samples show strong EPR signals of V_{Zn}^- and the S centre [20] in darkness at 295 K. Under illumination, the strong signal of the singly positively charged O vacancy (V_{O}^+) [21] was detected. Cooling down the sample from 295 K in darkness, a new EPR spectrum, labelled S1, appears at temperatures $T < 50\ \text{K}$, whereas the signals of the V_{Zn}^- and S centres become very weak (Fig. 1). For temperatures in the range of $\sim 50\text{-}120\ \text{K}$, the E doublet [18] was also weakly detected at slightly lower magnetic fields than S1. In none of our samples, the doublet D [18] was detected (neither in darkness nor under illumination).

For the magnetic field along the *c* direction ($\mathbf{B} \parallel \mathbf{c}$), the S1 spectrum consists of a doublet with a splitting of $\sim 2.3\ \text{G}$ which appears at almost the same position as the non-axial V_{Zn}^- spectrum [Fig. 1(a)]. For arbitrary directions of $\mathbf{B}$ in the $(11\bar{2}0)$ plane, the doublet splits into six doublets. For $\mathbf{B} \perp \mathbf{c}$, lines corresponding to equivalent orientations coincide and three doublets are observed [Fig. 1(b)]. Four of six doublets with anisotropic splitting show weak satellites with a similar splitting of $\sim 10.5\ \text{G}$ [Fig. 1(b)]. Such doublets appear as typical hyperfine (hf) structures due to the interaction between an electron spin $S=1/2$ and a nuclear spin $I=1/2$ of an impurity having close to 100% natural abundance of a single isotope. The weak satellites were only observed with the doublets that have anisotropic splitting, suggesting that they are related to forbidden transitions.

In a system with $S=1/2$ and $I=1/2$, forbidden transitions may become detectable in cases when the hf interaction between the electron spin and the nuclear spin is comparable or weaker than the nuclear Zeeman interaction between the nuclear spin and the external magnetic field. This may occur for impurities having a large nuclear g_n value. A typical example is the EPR spectra of the phosphorous shallow donors in SiC [22]. The splitting of ~ 10.5 G (or ~ 29.43 MHz) in the magnetic field range of ~ 3300 - 3360 G corresponds well to two times of the nuclear Zeeman frequency of ^1H ($\sim 14.90218 \times 2 \sim 29.80$ MHz at 3500 G). This strongly suggests that the observed doublet is the hf structure due to the interaction between an unpaired electron spin and a nuclear spin of ^1H ($I=1/2$, 99.985% natural abundance). We have noticed that the S1 signal is strongest in samples irradiated with an electron dose of $\sim 2 \times 10^{18} \text{ cm}^{-2}$ and becomes much weaker in heavier irradiated samples ($\sim 4 \times 10^{18} \text{ electrons/cm}^2$). This is expected for a defect involving an impurity since the defect concentration is limited by the impurity concentration.

Fig. 2 shows the angular dependence of the S1 spectrum measured at 30 K with $\mathbf{B}$ rotating in the $(11\bar{2}0)$ plane. When rotating $\mathbf{B}$ away from the c axis, the doublet splits into six doublets corresponding to six possible defect orientations with respect to the direction of the magnetic field. The observation of separated six doublets indicates low C_1 symmetry of the defect. For doublets labelled 2 and 5, the hf splitting is almost isotropic and no forbidden lines were observed (Fig. 2), whereas for other four doublets, the hf splitting is anisotropic and even changes the sign, showing crossing points in the angular dependence. The doublets with anisotropic splitting show a large variation in the line intensity and their forbidden lines were detected. This is typical for a dipolar interaction between two separated spins $S=1/2$ and $I=1/2$ [23]. The angular dependence, plotted as open circles in Fig. 2, can be described by the spin-Hamiltonian

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} - g_n \mu_n \mathbf{B} \cdot \mathbf{I}. \quad (1)$$

Here the first term describes the electronic Zeeman interaction, the second term represents the hf interaction and the last one is the nuclear Zeeman term. $\mathbf{g}$ and $\mathbf{A}$ are the g - and A -tensor, μ_B and μ_n are the Bohr and nuclear magneton, respectively, and g_n is the nuclear g value for ^1H ($g_n=5.5856912$). The spin-Hamiltonian parameters obtained from the best fit are given in Table 1. The simulations of the angular dependences of the main and forbidden lines using Eq. (1) and parameters in Table 1 are also plotted in Fig. 2 as solid and dashed curves, respectively. The excellent description of the angular dependence using the proton g -factor clearly indicates that S1 contains a single H atom. For an easy reference, the spin-Hamiltonian parameters of the non-axial V_{Zn}^- defect determined from measurements performed at 110 K are also given in Table 1.

In a system with an electron spin $\mathbf{S}$ and a nuclear spin $\mathbf{I}$, as in the case of the S1 centre, $\mathbf{S}$ induces an inductive field at the site of $\mathbf{I}$. A sudden change of the polarization of $\mathbf{S}$ (by the microwave field in ESEEM experiments) induces a change of the sign of this local field. The precession of the nuclear spin about the resultant nuclear precession field will then induce a change in the field at the site of $\mathbf{S}$. This acts as a field modulation, causing a slight difference in the precession frequency of the electron spin about the external magnetic field $\mathbf{B}$. Such a field modulation is known to have an effect on the ESE spectrum which can be detected by ESEEM [23]. From ESEEM, the nuclear Zeeman frequency can be directly deduced in a similar way as in electron nuclear double resonance (ENDOR) experiments [24].

Fig. 3(a) shows the two-pulse echo decay spectrum of the doublet 3 (see Fig. 2) measured at 20 K for $\mathbf{B}$ at the angle $\theta = 65^\circ$ from the c axis. The intensity of Hahn echo ($90^\circ - \tau - 180^\circ - \tau$ -echo) was measured as a function of the inter-pulse delay τ by using the microwave pulses sufficiently strong to excite all the allowed and forbidden lines of the doublet simultaneously and nonselective detection. After subtracting the slow decay due to the spin-relaxation processes, the time-domain spectrum in Fig. 3(a) was converted to the frequency-domain spectrum by Fourier transformation (FT) [Fig. 3(b)]. In the frequency-domain FT-ESEEM spectrum shown in Fig. 3(b), the second and the third frequencies correspond to the ENDOR frequencies ($|v_n - A/2|$ and $|v_n + A/2|$, respectively, with A is the hf splitting and v_n the nuclear Zeeman frequency), whereas the first and the fourth frequencies are the difference and the sum of the second and the third frequencies, respectively. With $|v_n - A/2| \sim 15.13$

MHz and $|v_n + A/2| \sim 15.78$ MHz, we obtain the hf splitting of $A \sim 0.65$ MHz, which is not resolved in the EPR spectrum, and the nuclear Zeeman frequency of $v_n \sim 15.45$ MHz. Within the experimental error, the obtained value v_n can be identified as the nuclear Zeeman frequency of ^1H (~ 14.90218 MHz at ~ 3500 G), confirming unambiguously the involvement of a single H atom in the S1 centre.

From the observed principal A-values and the directions of the principal axes (Table 1), it can be seen that the axis of the dipole is $\sim 78^\circ$ from the c axis ($\theta = 78.30^\circ$) and makes an angle of $\varphi \sim 21^\circ$ with the $[11\bar{2}0]$ direction. The low symmetry C_1 of the defect indicates that H is not on the substitutional site. The small hf splitting is an indication of negligible localization of the electron spin on H. The hf interaction is a pure anisotropic dipolar interaction as shown from the traceless A-tensor and the direction of the dipole is neither in $\{1\bar{1}00\}$ nor in $\{11\bar{2}0\}$ high-symmetric planes. Since the observed hf structure is purely from H as shown from ESEEM measurements, the involvement of other common impurities having a non-zero nuclear spin and a reasonable natural abundance (more than a few percentages), such as Li and common transition metals, in the S1 defect can be excluded. All these indicate that the electron spin is likely localized at an O atom. (The ^{17}O isotope with $I=5/2$ and the natural abundance of 0.038% is too low to be detected, whereas ^{67}Zn with $I=5/2$ and 4.1% should give rise to a detectable hf structure.) Moreover, the S1 centre is observed after electron irradiation which creates very high concentrations of vacancies. Therefore, the best defect model for S1 is a H^+ ion trapped at a V_{Zn}^- as illustrated in Fig. 4.

In this model, the H^+ ion saturates an O dangling bond in the basal plane [$\text{H}-\text{O}_3$ bond in Fig. 4(a)] but the unpaired electron spin is localized on the p -orbital of another O neighbour of V_{Zn} in the basal plane (either O_2 or O_4 in the figure), explaining the observed pure dipolar interaction. The low symmetry C_1 of the centre indicates that H is not at the substitutional Zn site. This is in line with the short O–H bond predicted by theoretical calculations (~ 1 Å [8,17]). The observed angles θ and φ of the principal z -axis of the hf tensor indicate that H atom is at the position so that the axis of the O_2 –H dipole will make angles of $\sim 78^\circ$ with the c -axis and of $\sim 21^\circ$ with the $\langle 11\bar{2}0 \rangle$ direction as illustrated in Fig. 4(b).

The formation of the OH bond along the c axis is predicted to occur [8]. In this case, we expect that the defect should also have low symmetry (not higher than C_{1h}). In the previous study by Evans and co-workers [18], the E and D doublets were assigned to H at V_{Zn} with the unpaired spin localized on a non-axial and axial O, respectively. The assignment of the D doublet as H-related was based on the observation of satellites which were believed to be the forbidden hf lines of the ^1H . The D doublet was not detected in all our samples (neither in darkness nor under illumination in the whole temperature range 5–295 K). Since no angular dependences of the D and E doublets [18] were reported, the comparison between S1 and the D and E centres is difficult. Unfortunately, the signal of the E doublet in our samples is too weak for a reliable study of the angular dependence. The presence of the R centre, which was previously assigned to V_{Zn}^- disturbed by a nearby Zn interstitial, $\text{V}_{\text{Zn}}^-:\text{Zn}_i^0$ [20], in the same magnetic field region of the E and non-axial V_{Zn}^- centres makes the study even more difficult. While the doublet structure of the E centre is an indication of the involvement of H, the lack of information on the direction of the dipolar interaction between the unpaired spin and the nuclear spin of H, makes it difficult to know if the E doublet can be a candidate for the axial or non-axial configuration of H at V_{Zn} . We have noticed that in darkness, the E doublet can only be detected at temperatures above 50 K when the S1 spectrum already disappeared. It is, therefore, possible that the E doublet is related to a metastable state of the S1 centre.

We observed no changes in the intensity of the EPR spectra of V_{Zn}^- , V_{O}^+ and S1 centres after annealing the sample at 100°C for 15 minutes in Ar flow ambient. After annealing at 200°C , no noticeable changes in the intensity of the V_{O}^+ spectrum could be observed, whereas the EPR spectra of V_{Zn}^- and S1 centres could not be detected (neither in darkness nor under illumination). Since the $\text{V}_{\text{Zn}}\text{H}_2$ defect is stable up to $\sim 500^\circ\text{C}$ [17], the disappearance of the V_{Zn}^- and S1 spectra may be due to the capture of H released from other less stable H-related donors at $\sim 200^\circ\text{C}$ [7], forming $\text{V}_{\text{Zn}}\text{H}_2$ or

other H-related EPR inactive complexes.

4. Summary

In summary, we have observed a new EPR spectrum S1 in ZnO after electron irradiation. From EPR and ESEEM data, the doublet S1 is unambiguously identified as due to the dipolar interaction between an unpaired electron and a nuclear spin of ^1H . The analysis of the g-tensor and the hf tensor suggests that S1 is an isolated H^+ ion trapped at a V_{Zn}^- , making a short O–H bond with only one O neighbour in the basal plane and forms a low symmetry C_1 defect while the unpaired electron spin localized on the p orbital of another O neighbour also in the basal plane of the vacancy. The partly and fully H passivated V_{Zn} defects are more stable than the H interstitials and, hence, can be the dominant H-related defect in ZnO. Similar defects can be common for H at a cation vacancy also in other oxide semiconductors.

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Table 1. The g- and A-tensor, their principal values and the polar angle θ and azimuthal angle ϕ of the principal axes, of the S1 centre in ZnO. The angles $\theta = 0$ and $\phi = 0$ correspond to the [0001] and $[11\bar{2}0]$ directions, respectively. The principal A-values are given in 10^{-4} cm^{-1} (the corresponding values in MHz using the conversion factor $A[\text{MHz}] = 2.99792453684A[10^{-4} \text{ cm}^{-1}]$ are also given in parentheses) and the angles θ and ϕ are measured in degrees. For an easy reference, the spin-Hamiltonian parameters of the non-axial V_{Zn}^- determined from measurements performed at 110 K are also given. The maximum errors in determination of the g- and A-values are ± 0.0003 and $\pm 0.2 \times 10^{-4} \text{ cm}^{-1}$, respectively.

Center	Parameters	Matrix elements			Principal value		θ	ϕ
S1 (C_1)	g	2.0120	0.0146	-0.0064	1	2.0077	67.57	353.43
			2.0464	-0.0244	2	2.0648	117.42	71.07
				2.0163	3	2.0023	36.73	117.02
	A	-3.316	-2.250	-1.015	1	-4.4 (13.2)	78.30	21.15
			1.838	-0.756	2	2.8 (8.4)	107.64	107.38
				1.478	3	1.6 (4.8)	21.38	143.07
V_{Zn}^- (C_{1h})	g	2.0053	0	0.0046	1	2.0036	110.21	0
			2.0185	0	2	2.0185	90.00	90.00
				2.0161	3	2.0178	20.21	0

Figure 1. (Colour online) EPR spectra in electron-irradiated ZnO measured in darkness at 30 K for (a) $\mathbf{B} \parallel \mathbf{c}$ and (b) $\mathbf{B} \perp \mathbf{c}$ ($\mathbf{B} \parallel [1\bar{1}00]$), showing the small-splitting doublet S1. For some doublets, weak satellites corresponding to forbidden transitions with a splitting of ~ 10.5 G were detected. The magnetic field modulation is 0.2 G.

Figure 2. (Colour online) Angular dependence of S1 measured at 30 K with $\mathbf{B}$ rotating in the $(11\bar{2}0)$ plane ($\theta=0^\circ$ and $\theta=90^\circ$ correspond to $\mathbf{B} \parallel [0001]$ and $\mathbf{B} \parallel [1\bar{1}00]$, respectively) showing six separated doublets corresponding to six unequivalent defect orientations (with respect to the magnetic field) of a low symmetry C_1 centre. The open circles denote the experimental data of the resonance positions, whereas the solid and dotted curves represent the simulations of the main and forbidden lines, respectively, using the spin-Hamiltonian Eq. (1) and parameters in Table 1.

Figure 3. Two-pulse ESEEM spectrum measured at 20 K on the lowest field line of S1 at the angle $\theta = 65^\circ$ from the c axis ($B = 3365.76$ G at the microwave frequency of 9.7209 GHz): (a) time-domain spectrum showing the modulation of the nuclear spin on the ESE signal, and (b) its Fourier transformed frequency-domain spectrum showing the allowed and forbidden transitions. The frequencies are shown in parentheses in MHz.

Figure 4. (Colour online) Model of the S1 defect: an isolated H^+ at a V_{Zn}^- see from (a) the $[0001]$ direction and (b) a $\langle \bar{1}100 \rangle$ direction. H makes a short O–H bond with only one O atom in the basal plane and the unpaired electron spin localizes on another O neighbour also in the basal plane of the vacancy.