Hydrogen at zinc vacancy of ZnO: an EPR and ESEEM study

Nguyen Tien Son, J. Isoya, Ivan Gueorguiev Ivanov, T. Ohshima and Erik Janzén

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Nguyen Tien Son, J. Isoya, Ivan Gueorguiev Ivanov, T. Ohshima and Erik Janzén, Hydrogen at zinc vacancy of ZnO: an EPR and ESEEM study, 2014, INTERNATIONAL CONFERENCE ON DEFECTS IN SEMICONDUCTORS 2013, 341-344.

<http://dx.doi.org/10.1063/1.4865666>

Copyright: © 2014 AIP Publishing LLC

<http://scitation.aip.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-111622>

Hydrogen at zinc vacancy of ZnO: An EPR and ESEEM study

N. T. Son, J. Isoya, I. G. Ivanov, T. Ohshima, and E. Janzén

Citation: [AIP Conference Proceedings](#) **1583**, 341 (2014); doi: 10.1063/1.4865666

View online: <http://dx.doi.org/10.1063/1.4865666>

View Table of Contents: <http://scitation.aip.org/content/aip/proceeding/aipcp/1583?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Size effects on formation energies and electronic structures of oxygen and zinc vacancies in ZnO nanowires: A first-principles study](#)

J. Appl. Phys. **109**, 044306 (2011); 10.1063/1.3549131

[Zinc and oxygen vacancies in ZnO nanorods](#)

J. Appl. Phys. **106**, 104307 (2009); 10.1063/1.3259413

[Further characterization of oxygen vacancies and zinc vacancies in electron-irradiated ZnO](#)

J. Appl. Phys. **103**, 043710 (2008); 10.1063/1.2833432

[Identification of oxygen and zinc vacancy optical signals in ZnO](#)

Appl. Phys. Lett. **89**, 262112 (2006); 10.1063/1.2424641

[Oxygen vacancies in ZnO](#)

Appl. Phys. Lett. **87**, 122102 (2005); 10.1063/1.2053360

Hydrogen at zinc vacancy of ZnO: an EPR and ESEEM study

N. T. Son^a, J. Isoya^b, I. G. Ivanov^a, T. Ohshima^c, and E. Janzén^a

^aDepartment Physics, Chemistry and Biology, Linköping University, SE-58183 Linköping, Sweden

^bGraduate School of Library, Information & Media Studies, University of Tsukuba, Tsukuba, Ibaraki 305-8550, Japan

^cJapan Atomic Energy Agency, Takasaki, Gunma 370-1292, Japan

Abstract. An electron paramagnetic resonance (EPR) spectrum, labeled S1, with small-splitting doublet accompanied by weak satellites is observed in ZnO irradiated with 2 MeV electrons. The obtained structure is shown to be the hyperfine structure due to the dipolar interaction between an unpaired electron spin and a nuclear spin of hydrogen (H). The observation of the nuclear Zeeman frequency of H in electron spin echo envelope modulation experiments further confirmed the presence of a hydrogen atom in S1. From the observed spin-Hamiltonian parameters, S1 is identified to be the partly H-passivated Zn vacancy, $V_{\text{Zn}}^- \text{H}^+$, with the H^+ ion making a short O-H bond with only one nearest O neighbor of V_{Zn} in the basal plane, being off the substitutional site, while the unpaired electron spin, which gives rise to the observed EPR signal, is localized on the p orbital of another O neighbor also in the basal plane.

Keywords: ZnO, hydrogen, vacancies, hyperfine interaction, electron paramagnetic resonance.

PACS: 71.55.Gs, 76.30.Lh, 61.72.Hh, 61.72.jd

INTRODUCTION

Hydrogen is known to be present in ZnO grown by any method. Calculations predicted that the formation energy of the interstitial H^+ is low enough to allow a large concentration of H in as-grown ZnO.¹ In the bond-center configurations, H_{BC} , hydrogen interstitials act as shallow donors and have been suggested to be the source for the natural n-type doping in as-grown ZnO.¹ The H_{BC} centers were later identified by infrared (IR) spectroscopy.^{2,3} Hydrogen-related shallow donors have also been identified by muon spin rotation⁴ and electron paramagnetic resonance (EPR).⁵ The isolated H at an O vacancy, H_{O} , was predicted to bond equally with all nearest Zn neighbors, forming a multi-bond center⁶ or to occur simply as an anion H^- at the anion O site.⁷ The prediction on H_{O} was later supported by IR absorption.³ The isolated H interstitials are predicted to have low migration energies (~ 0.5 eV for different configurations of H_{BC}) and can become mobile at room temperature.⁸ More thermally stable H-related defects are therefore expected to be H interstitials trapping at acceptor impurities^{9,10,11} or interstitial H_2 molecules.¹² The H passivation of intrinsic acceptors, such as the Zn vacancy (V_{Zn}) in n-type ZnO, is also predicted to be highly energetically favorable, forming the partly ($V_{\text{Zn}}\text{H}$) and fully ($V_{\text{Zn}}\text{H}_2$) H-passivated V_{Zn} defects.⁸ The $V_{\text{Zn}}\text{H}_2$ complex was suggested to be the defect model for the H-II center observed by IR spectroscopy.² In EPR studies of electron-irradiated ZnO by Evans and co-workers¹³ the doublets D and E were suggested to be related to the axial and non-axial configurations of $V_{\text{Zn}}^- \text{H}^+$.

In the present study, a new EPR doublet spectrum is observed in electron-irradiated ZnO. From the spin-Hamiltonian parameters observed by EPR, the doublet is identified to be the $V_{\text{Zn}}^- \text{H}^+$ defect. The involvement of a H atom in the defect is further confirmed by the observation of the nuclear Zeeman frequency of ^1H by electron spin echo envelope modulation (ESEEM). The microscopic model of the defect is discussed.

EXPERIMENT

Samples used in this study are nominally undoped ZnO substrates from Tokyo Denpa which have the resistivity in the range of ~ 500 - $1000 \Omega\text{cm}$. The irradiation by 2 MeV electrons was performed at room temperature to doses ~ 2 - $4 \times 10^{18} \text{ cm}^{-2}$. Continuous-wave EPR measurements were performed on a Bruker ELEXSYS E500 X-band (~ 9.45 GHz) spectrometer. Electron spin echo (ESE) detected EPR and ESEEM experiments were performed on a Bruker ELEXSYS E580 X-band (~ 9.75 GHz) spectrometer. Both spectrometers are equipped with Oxford continuous He-

flow cryostats, allowing the regulation of the sample temperature in the range of 4–295 K. In the pulsed experiments, the echo intensity was obtained by integrating the echo signal within the range of the gate centered on the top of the echo. By changing the width of the gate, either non-selective detection, which collects responses from all the signals within the excitation bandwidth of the microwave pulses, or a selective detection, which virtually eliminates the contribution from off-resonance signals, is chosen. In the echo-detected EPR, the intensity of Hahn-echo ($90^\circ - \tau - 180^\circ - \tau$ -echo) was measured as a function of the external magnetic field strength B . For ESEEM measurements, a similar two-pulse sequence was used and the echo intensity was measured as a function of time.

RESULTS AND DISCUSSION

Figure 1 shows the EPR spectra in ZnO after irradiation by 2 MeV electrons at room temperature to a dose of $2 \times 10^{18} \text{ cm}^{-2}$ measured in darkness at 20 K. For the magnetic field $\mathbf{B}$ along the c axis ($\mathbf{B} \parallel \mathbf{c}$), the spectrum shows a dominating doublet, labelled S1, and weak signals of the S center¹⁴ and the negative Zn vacancy, V_{Zn}^- , in non-axial configuration¹⁵ and Mn^{2+} (Ref. 16) [Fig. 1(a)]. The doublet splits into six doublets when rotating the magnetic field away from the c axis as can be seen in the spectrum measured at an angle $\theta \sim 65^\circ$ [Fig. 1(b)]. Four doublets, labeled 1, 3, 4 and 6, have weak satellites with a similar splitting of ~ 10.5 G. These satellites are not observed for doublets 2 and 5 [Fig. 1(b)]. The appearance of weak satellites and the variation of the intensity between the doublets are typical features of a system having an electron spin $S=1/2$ and a nuclear spin $I=1/2$ with the nuclear Zeeman interaction comparable to the hyperfine (hf) interaction. This has been observed for shallow impurities having large nuclear g -values, such as the phosphorous shallow donors in 4H- and 6H-SiC.¹⁷ The satellites are related to the forbidden transitions of the system $S=1/2$, $I=1/2$, which become partly allowed when the relative strength between the hf interaction and the nuclear Zeeman interaction changes. The splitting of the forbidden lines corresponds to the two times of the nuclear Zeeman frequency ($2\nu_N$) of the involved impurity. In this case, $2\nu_N \sim 10.5$ G or ~ 29.43 MHz which is very close to the two times nuclear Zeeman frequency of ^1H [$2\nu_N(\text{H}) \sim 29.80$ MHz at 3500 G or ~ 28.52 MHz at 3350 G]. This indicates that the S1 doublet is related to H.

We found that the angular dependence of the doublet S1, including the forbidden lines, with the magnetic field rotating in the $(11\bar{2}0)$ plane can be well 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

FIGURE 1. (Color online) EPR spectra of S1 in electron-irradiated ZnO measured in darkness at 20 K for (a) $\mathbf{B} \parallel \mathbf{c}$ and (b) $\mathbf{B}$ is in the $(11\bar{2}0)$ plane and $\sim 65^\circ$ away from the c axis, showing the doublet structure with the splitting varying in the range of ~ 2.4 – 3.5 G. At an arbitrary angle of the magnetic field, the doublet is split into six ones. All the doublets, except the ones labeled 2 and 5, have two weak satellites with a splitting in the range of ~ 10.5 G. The field modulation is 0.2 G. The intensity of the spectrum in (a) is reduced by 20 times

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 center 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) while θ and ϕ are measured in degrees. The maximum errors in determination of the principal g- and A-values are ± 0.0003 and $\pm 0.2 \times 10^{-4} \text{ cm}^{-1}$, respectively.

Parameters	Matrix elements			Principal value		θ	ϕ
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

last one is the nuclear Zeeman term. **g** and **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 ($g_n=5.5856912$). It is noticed that the forbidden lines can only be fitted using the g_n value for ^1H . Thus, the involvement of a H atom in the S1 defect is unambiguously confirmed. The obtained spin-Hamiltonian parameters for S1 are given in Table 1.

In a system with an electron spin **S** and a nuclear spin **I**, as in the case of S1, **S** induces an inductive field at the site of **I**. A sudden change of the polarization of **S** (by the microwave field in ESEEM experiments) induces a change of the sign of this local field. The precession of **I** about the resultant nuclear precession field will then induce a change in the field at the site of **S**. This acts as a field modulation, causing a slight difference in the precession frequency of the electron spin about the external magnetic field **B**. Such a field modulation is known to have an effect on the ESE spectrum which can be detected by ESEEM.¹⁸ From ESEEM experiments, the nuclear Zeeman frequency can be directly deduced in a similar way as in electron nuclear double resonance (ENDOR) experiments.¹⁹

We performed ESEEM experiments on the weak doublet 3 in Fig. 1(b). Fig. 2 shows the frequency-domain ESEEM spectrum obtained from Fourier transform of the time-domain ESEEM spectrum measured at 20 K. As can be seen in the figure, four frequencies, labeled 1-4, are observed. Here, lines 2 and 3 correspond to the allowed transitions with the frequencies $|v_N - A/2|$ and $|v_N + A/2|$ with A is the hf splitting and v_N the nuclear Zeeman frequency, while lines 1 and 4 correspond to the difference (A) and the sum ($2v_N$) of the two allowed frequencies, respectively. Thus, line 4 corresponds to $2v_N \sim 30.91 \text{ MHz}$. This value is close to the two times of the nuclear Zeeman frequency of ^1H ($2v_N(\text{H}) \sim 29.80 \text{ MHz}$ at 3500 G). This observation thus unambiguously confirms the involvement of a hydrogen atom in the S1 defect, further supporting the EPR identification. Also, the involvement of any impurity with $I \neq 0$ and a reasonable natural abundance of a few percentages or larger, such as Li or common transition metals, in S1 can be excluded (otherwise their nuclear Zeeman frequencies should be detected in ESEEM).

From the observed g-tensor, it is clear that the S1 defect has low symmetry C_1 . This suggests that H is not at the

FIGURE 2. Two-pulse ESEEM frequency-domain spectrum measured at 20 K on doublet 3 of S1 in Fig. 1(b) at the angle $\theta \sim 65^\circ$ from the c axis ($B = 3365.76 \text{ G}$ at the microwave frequency of 9.72029 GHz) showing the allowed and forbidden transitions. The frequencies are shown in parentheses in MHz.

substitutional site. The very small hf constants, as shown in Table 1, and the traceless hf A-tensor (i.e., $A_1 + A_2 + A_3 = 0$) indicate that H does not carry the electron spin and the hf interaction is a pure dipolar interaction with the axis of the dipole along the axis of A_1 [$A_{||} = A_1$, and $A_{\perp} = (A_2 + A_3)/2$]. This means that the unpaired electron should be localized on the p orbital of an atom having a nuclear spin $I=0$. It is likely that the unpaired electron is localized at an O atom, since the only O isotope having $I \neq 0$ is ^{17}O ($I=5/2$) which has too low natural abundance (0.038%) to be detectable. (If the unpaired electron spin is on a Zn atom, then the hf interaction with ^{67}Zn ($I=5/2$ and 4.1% natural abundance) should give rise to a detectable hf structure.) Moreover, the S1 center is observed after electron irradiation which creates high concentrations of vacancies. Therefore, the best defect model for S1 is a positive H^+ ion trapped at a negative Zn vacancy V_{Zn}^- . The observed Euler angles of the dipole (along the axis of A_1) $\theta \sim 78^\circ$ with the c axis and $\phi \sim 21^\circ$ with the $\langle 11\bar{2}0 \rangle$ direction suggest that the unpaired electron should be on one of three O atoms in the basal plane, while H makes a short O-H bond with another O neighbor V_{Zn}^- also in the basal plane, forming a low symmetry C_1 defect.

The D and E centers were previously assigned to the axial and non-axial configurations of $\text{V}_{\text{Zn}}^- \text{H}^+$, respectively, by Evans and co-workers.¹³ The assignment of D as a H-related center was based only on the observation of two weak satellites with a splitting of ~ 11 G, which is close to the two times of the nuclear Zeeman frequency of ^1H . However, neither the symmetry nor parameters of these two centers were determined (only a single EPR spectrum measured at the c direction was reported).¹³ The E center was observed in all our samples, while the D doublet could not be detected in the whole temperature range of 5-295 K (neither in darkness nor under illumination). It is noticed that in darkness the E spectrum can only be detected at temperatures above 50 K when the S1 signal disappears. Due to lack of data, it is not clear whether the E center is also related to H and if it can be a candidate for the axial configuration or an excited state of the $\text{V}_{\text{Zn}}^- \text{H}^+$ defect.

In summary, we have observed an EPR doublet, S1, in electron-irradiated ZnO. It is suggested from EPR and ESEEM experiments that S1 is a positive H^+ ion trapped at an O neighbor of a negative Zn vacancy V_{Zn}^- in the basal plane, making a short O-H bond, while the unpaired electron spin is localized on the p orbital of another O neighbor of V_{Zn}^- also in the basal plane, forming a low symmetry C_1 defect.

ACKNOWLEDGMENTS

Support from the Linköping Linnaeus Initiative for Novel Functional Materials (VR) and the Knut and Alice Wallenberg Foundation is gratefully acknowledged.

REFERENCES

1. C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012-1015 (2000).
2. E. V. Lavrov, J. Weber, F. Börmert, C. G. Van de Walle, and R. Helbig, Phys. Rev. B **66**, 165205 (2002).
3. E. V. Lavrov, F. Herklotz, and J. Weber, Phys. Rev. B **79**, 165210 (2009).
4. S. F. J. Cox, E. A. Davis, S. P. Cottrell, P. J. C. King, J. S. Lord, J. M. Gil, H. V. Alberto, R. C. Vilão, J. Piroto Duarte, N. Ayres de Campos, A. Weidinger, R. L. Lichti, and S. J. C. Irvine, Phys. Rev. Lett. **86**, 2601-2604 (2001).
5. D. M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B. K. Meyer, S. Orlinskii, J. Schmidt, and P. G. Baranov, Phys. Rev. Lett. **88**, 045504 (2002).
6. A. Janotti and C. G. Van de Walle, Nat. Mater. **6**, 44-47 (2007).
7. H. Takenaka and D. J. Singh, Phys. Rev. B **75**, 241102(R) (2007).
8. M. G. Wardle, J. P. Goss, and P. R. Briddon, Phys. Rev. Lett. **96**, 204504 (2006).
9. E. V. Lavrov, F. Herklotz, and J. Weber, Phys. Rev. B **79**, 165210 (2009).
10. G. A. Shi, M. Stavola, and W. B. Fowler, Phys. Rev. B **73**, 081201(R) (2006).
11. S. J. Jokela and M. D. McCluskey, Phys. Rev. B **76**, 193201 (2007).
12. G. A. Shi, M. Saboktakin, M. Stavola, and S. J. Pearton, Appl. Phys. Lett. **85**, 5601-5603 (2004).
13. S. M. Evans, N. C. Giles, L. E. Halliburton, and L. A. Kappers, J. Appl. Phys. **103**, 043710 (2008).
14. D. Galland and A. Herve, Phys. Lett. **33A**, 1-2 (1970).
15. B. Schallenger and A. Hausmann, Z. Phys. B **23**, 177-181 (1976).
16. P. B. Dorain, Phys. Rev. **112**, 1058-1060 (1958).
17. N. T. Son, A. Henry, J. Isoya, M. Katagiri, A. Gali, and E. Janzén, Phys. Rev. B **73**, 075201 (2006).
18. L. G. Rowan, E. L. Hahn, and W. B. Mims, Phys. Rev. **137**, A61-A71 (1965).
19. J. Isoya, M. K. Bowman, J. R. Norris, and J. A. Weil, J. Chem. Phys. **78**, 1735-1746 (1983).