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Defects at nitrogen site in electron-irradiated AIN

N. T. Son, $^{1,a)}$ A. Gali, 2,3 Á. Szabó, 3 M. Bickermann, 4 T. Ohshima, 5 J. Isoya, 6 and E. Janzén 1

¹Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden ²Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

³Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1111 Budapest, Hungary

⁴Department of Materials Science 6, University of Erlangen–Nürnberg, Martensstrasse 7, D-91058 Erlangen, Germany

²Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

⁶Graduate School of Library, Information and Media Studies, University of Tsukuba, Tsukuba, Ibaraki 305-8550, Japan

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In high resistance AlN irradiated with 2 MeV electrons, an electron paramagnetic resonance (EPR) spectrum, labeled EI-1, with an electron spin S=1/2 and a clear hyperfine (hf) structure was observed. The hf structure was shown to be due the interaction between the electron spin and the nuclear spins of four ²⁷A nuclei with the hf splitting varying between ~6.0 and ~7.2 mT. Comparing the hf data obtained from EPR and *ab initio* supercell calculations we suggest the EI-1 defect to be the best candidate for the neutral nitrogen vacancy in AlN. © 2011 American Institute of Physics. [doi:10.1063/1.3600638]

In recent years, considerable progress in crystal growth and in *n*-type and *p*-type doping of aluminum nitride (AlN) has led to the fabrication of light emitting diodes in deep ultraviolet (UV) spectral region¹ and made the material more promising for deep-UV laser applications. However, doping is still a serious problem for AlN and its alloy AlGaN with high Al content. Nominal undoped AlN grown by either metalorganic chemical vapor deposition or physical vapor transport (PVT) is semi-insulating. This is generally believed to be due to carrier compensation by deep level defects such as residual oxygen at N site (O_N) and/or the N vacancy (V_N) donor centers in the case of *p*-type doping or the Al vacancy (V_{Al}) acceptor center in the case of *n*-type doping. The V_N (or V_{Al}) has been predicted by theory to have low formation energies in *p*-type (or *n*-type) AlN and is expected to be abundant in as-grown materials.^{2–4} The calculations also suggested that V_N transforms from a shallow donor in GaN to a deep donor in AlN and compensates acceptors, making *p*-type doping of AlN difficult. So far, no conclusive experimental identification of vacancies in AlN has been reported. In neutron-irradiated polycrystalline AlN, a broad electron paramagnetic resonance (EPR) signal with g=2.007 was assigned to V_N.^{5,6} In as-grown AlN, a number of optical detection of EPR spectra were observed but non of them showed a resolved hyperfine (hf) structure and hence could not be identified.⁷ In a more recent study of as-grown AlN, an EPR spectrum with an unresolved hf structure due to the interaction with 27 Al nuclei (nuclear spin I=5/2 and 100% natural abundance) was observed and assigned to either the neutral N vacancy (V_N^0) or the shallow O_N donor.⁸

In this letter, we report our observation of an EPR spectrum with an electron spin S = 1/2 and a clear hf structure in AlN after electron irradiation. The structure is shown to be due to the hf interaction between the electron spin and the

nuclear spins of four ²⁷Al nuclei. Comparing the ²⁷Al hf data obtained from EPR and *ab initio* calculations we suggest the defect to be the best candidate for V_N^0 in AlN.

The samples used in our study are bulk AlN grown by PVT. The irradiation with 2 MeV electrons was performed at \sim 300 K with doses $\sim 2-10 \times 10^{18}$ cm⁻³. EPR measurements were formed on X-band (~9.5 GHz) Bruker E500 and E580 spectrometers using a continuous flow cryostat, allowing sample temperature regulation in the range 4–295 K.

In as-grown AlN, an isotropic EPR signal at ~ 338 mT corresponding to a g-value of ~ 2.009 was observed in darkness in a wide range of temperature (4–295 K). Figure 1(a) show this spectrum measured at 20 K for the magnetic field along the c-axis (**B**||**c**). After electron irradiation, this line



FIG. 1. EPR spectra observed in darkness (a) in as-grown AlN and (b-d) in electron-irradiated AlN at different temperatures. The isotropic signal at \sim 338 mT in (a) and (b) is from an unidentified defect.

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^{a)}Electronic mail: son@ifm.liu.se.



FIG. 2. (Color online) EPR spectra (in gray) measured in irradiated AlN in darkness at 92 K for (a) **B**||**c**, (b) **B** is 40° off the c-axis, and (c) **B** \perp **c** after subtracting the isotropic signal in Fig. 1(b). The simulated spectra (indicated by arrows) assuming the hf interaction with two pairs of equivalent ²⁷Al neighbors having the corresponding hf splittings of: (a) 6.5 mT and 6.7 mT, (b) 6.5 mT for one pair of ²⁷Al neighbors and 6.0 mT and 7.2 mT for each of other two ²⁷Al atoms, and (c) 6.0 mT and 7.05 mT for each pairs. The spectra were simulated with g=2.012 and the Gaussian line shape with a line width of 2.4 mT.

does not seem to be affected but the broad signal overlapping with this line at the low-field side is reduced [Fig. 1(b)]. At temperatures above 80 K, a new spectrum, labeled EI-1 (EI: electron irradiation), with a hf structure consisting of 19 hf lines of nearly equal splitting (~6.6 mT) was observed. Figures 1(c) and 1(d) show this spectrum measured in darkness at 92 K for $B \parallel c$ and $B \perp c$, respectively.

Figure 2 shows the measured spectra (in gray) for different directions of the magnetic field as follows: (a) $\mathbf{B} \| \mathbf{c}$ (denoted as 0°), (b) **B** is 40° off the c-axis, and (c) $\mathbf{B} \perp \mathbf{c}$ (90°). In these spectra, the isotropic signal at \sim 338 mT shown in Fig. 1(b) was subtracted. The angular dependence study with **B** rotating in the (1120) plane shows that the hf lines are nearly isotropic but their relative peak intensity changes with the angle of the magnetic field as can be seen in Figs. 2(a)-2(c). The spectrum in Fig. 2(a) shows a rhombic shaped envelope typical for a hf interaction with a number of equivalent nuclei. In AlN, both 14N (I=1, 100% natural abundance) and ²⁷Al have nonzero nuclear spins. Our simulation shows that the hf interaction with four equivalent ²⁷Al nuclei with I=5/2 gives rise to 21 hf lines with the intensity ratio: 1:4:10:20:35:45:79:103:124:140:144:140:124:103:79: 45:35:20:10:4:1. This gives rise to a hf structure with the rhombic shaped envelope. The largest splitting lines with the intensity ratio of 1 are too weak to be distinguished from the noise level and therefore the observed spectra show 19 hf lines. The hf interaction with four equivalent ¹⁴N nuclei (I =1) would result in only 9 hf lines. We therefore believe that the EI-1 spectrum is related to a defect at N site and has the hf interaction with four nearest ²⁷Al neighbors. Since only the peak intensity of the hf lines and the envelope shape of the hf structure are markedly changed with the magnetic field direction while the angular variation in the line position is small (see Fig. 2), we can conclude that the anisotropy of the hf interaction should be smaller than the line width (~2.6 mT). In this case, the anisotropy of the hf interaction could not be studied from the angular dependence of the line position but can still be estimated from fitting of the hf structures at different crystal directions. The angular variation in EPR lines caused by the anisotropy of the g-value is within the line width and cannot be determined. Since the anisotropy of the g-value of intrinsic defects in semiconductors is usually small (~0.1% or less) we neglected the anisotropy of the g-value and used the value corresponding to the center of the hf structure (g=2.012) in the hf fitting.

In the case of a C_{3v} center, the Al atom along the c-axis moves away from the vacancy site and the spin density located in the dangling bond of this atom is often larger than that at one of the other three equivalent atoms in the basal plane. For $\mathbf{B} \| \mathbf{c}$, it is expected to observe two sets of hf lines corresponding to the interaction (i) with one Al atom along the c-axis having C_{3v} symmetry with a larger hf splitting and (ii) with three equivalent Al atoms in the basal plane having C_{1h} symmetry with smaller hf splittings. In the case of a C_{1h} center, reconstructed bonds are formed and the hf interactions with the pairs of atoms in the basal or vertical planes also give rise to two sets of hf lines both having C_{1h} symmetry. However, without dangling bonds, there is no atom with preferential spin localization and the hf splittings are expected to be less anisotropic. We found that the hf structure at $\mathbf{B} \| \mathbf{c}$ can be fitted if hf splittings are in the range 6.5–6.7 mT for C_{1h} symmetry or 6.5–6.9 mT for C_{3v} symmetry. Indeed, the hf structure in Fig. 2(a) has an envelope close to a rhombic shape. The simulated spectrum for C_{1h} symmetry with splitting of 6.5 and 6.7 mT for two pairs of equivalent Al atoms is shown in Fig. 2(a). With increasing the hf splitting of one Al atom from 6.9 to 7.2 mT (for C_{3n} symmetry), the deviation in line position of outer hf lines increases to 0.5-0.7 mT. This also causes a deviation in the intensity ratio of hf lines from the case of the interaction with four equivalent Al neighbors and the simulated spectrum shows a clear parallelogram-shaped envelope similar to the spectrum in Fig. 2(b). For $\mathbf{B} \perp \mathbf{c}$, the C_{1h} symmetry should give rise to two sets of hf lines for each pair and in total four sets of hf lines are expected. However, we found that the spectra can be very well fitted with two sets of hf lines with the splitting of 6.0 and 7.05 mT [Fig. 2(c)]. Using four sets of hf lines with 0.1–0.2 mT different in the hf splitting, i.e., $6.0 \pm (0.1 - 0.2)$ mT and $7.05 \pm (0.1 - 0.2)$ mT, does not improve the fit. The fit gets worse when changing the splitting of the two sets by more than 0.2 mT. This indicates that the difference in hf splitting of two pairs of Al atoms is within ${\sim}0.2\,$ mT. In the intermediate angles between 0° and 90° in the (1120) plane, each hf line will split into four lines due to C_{1h} symmetry. Assuming that the two sets of the hf lines corresponding to two pairs of Al atoms are also similar (within 0.2 mT), we could fit all the observed spectra. Figure 2(b) shows the simulated spectrum for the angle of 40° off the c-axis using the hf splitting of: 6.5 mT for double sites (corresponding to the interaction with two Al atoms) and 6.0 mT and 7.2 mT for each single site (corresponding to the interaction with one Al atom). These ²⁷Al hf splittings, 6.0 and 7.2 mT, were found to be the smallest and largest, respectively, among the observed values. We can therefore estimate the principal values of the hf tensors of the two pairs of Al atoms to be about: $A_{xx} \sim A_{yy} \sim 6.0 \pm 0.2$ mT and $A_{zz} \sim 7.2 \pm 0.2$ mT. The spectra in between 40° and 45° are

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TABLE I. Principal values (in mT) of the hf tensors for two pairs of ²⁷Al neighbors (Al₁, Al₄ and Al₂, Al₃) obtained from calculations for V_N^0 and estimated from EPR for the EI-1 defect. θ and φ are the polar and azimuthal angles measured in degree, respectively, of the principal axes of the A tensors. The difference values for atoms in the same pair are due to error in the calculation (~0.3 mT). The error of the A-values estimated from EPR is in the similar range.

Center	Atom	A _{xx}	A _{yy}	A _{zz}	θ	arphi
$\overline{V^0_N}$	Al	6.7	6.7	8.2	44.0	90.0
	Al ₂ Al ₃	5.9 5.9	6.0 6.0	7.5 7.6	89.3 90.9	-177.0 177.2
	Al_4	6.4	6.5	8.0	20.6	90.1
EI-1	Al_{1-4}	~6.0	~6.0	~7.2	~40-45	

rather similar and can be well fitted with the same hf parameters. The direction of the principal axes of hf tensors of the two Al pairs should be close to $\sim 40^{\circ} - 45^{\circ}$ off the c-axis. The estimated hf parameters are given in Table I. The hf structures at intermediate angles can also be fitted assuming C_{3v} symmetry for the center with the hf splitting varying in the same range (6.0–7.0 mT). However, the hf interaction with four nearly equivalent Al neighbors is typical for a defect with C_{1h} and not C_{3v} symmetry.

Since the EI-1 spectrum was only observed after electron irradiation, the associated defect is likely to be intrinsic. The hf interaction with four Al neighbors indicates that the defect is at N site and can be related to the N vacancy. With the effective electron spin S=1/2, the charge state of the N vacancy is expected to be neutral. However, V_N^0 has already been suggested as a possible model for another EPR center with C_{3v} symmetry by Evans *et al.*⁸

We modeled V_N in a 432-atom hexagonal AlN supercell using a Γ -point sampling of the Brillouin zone. This model worked very well for other defects in AlN.⁹ We applied density functional theory calculations by choosing the Perdew-Burke-Ernzerhof (PBE) functional.¹⁰ Plane waves with a cut-off of 420 eV were utilized for the valence electrons together with PAW potentials.¹¹ The geometry optimization was carried out by VASP code¹² while the hf tensors were determined by the CPPAW code.¹³ The V_N defect introduces levels in the fundamental band gap. The corresponding states show a_1, a_1 , and e characters in the unrelaxed case under C_{3v} point group where the first a_1 level is an s-like whereas the second a_1 and *e* levels are *p*-like contribution of the Al dangling bonds split in the hexagonal crystal field. In the neutral charge state the first a_1 level is fully occupied and it is very close to the valence band edge. Because the calculated PBE band gap is too small (4.0 eV), therefore the second a_1 and the e levels are relatively close to the conduction band (CB) edge. However, these states are very localized and distinct from the delocalized CB states, so they presumably represent deep levels in the fundamental band gap. The second a_1 level is singly occupied in the neutral charge state, so V_N^0 is paramagnetic. If C_{3v} point group is preserved during geometry optimization then the neighbor Al atom of the vacancy along the c-axis moves farther from the vacant site. As a consequence, the spin density will be primarily localized on the dangling bond of this single Al-atom while the rest is mostly distributed among the other three neighbor Al-atoms in the

basal plane. The singly occupied second a_1 level and the empty *e* levels are separated by about 0.5 eV, so this a_1 level will be clearly separated from the CB edge by about 0.7 eV even in PBE calculation. This configuration is metastable. We found that if two Al-atoms in the basal plane move closer to each other by distorting the symmetry of the defect to C_{1h} then the spin density distribution among the four Al-atoms near the vacant site will be almost equal. During this pairwise reconstruction the distances between the closest second neighbor Al atoms are around 2.94 Å. In this case the singly occupied a' level shifts down in the gap by about 0.23 eV compared to the counterpart a_1 level in C_{3v} configuration which stabilizes the C_{1h} configuration over the C_{3v} configuration by about 0.14 eV. This is a significant energy difference, thus we provide the hf tensors of neighbor ²⁷Al isotopes only for the most stable C_{1h} configuration.

As can be seen in Table I, the calculated principal ²⁷Al hf values are in good agreement with the experimental values estimated from EPR for the EI-1 defect. These hf parameters are completely different from that obtained for the C_{3v} center by Evans and co-workers⁸ (A_{II}=111.3 MHz~3.97 mT and A_⊥=54.19 MHz~1.93 mT for the Al atom long the c-axis and much smaller for other Al atoms in the basal plane). We therefore suggest the EI-1 defect to be the better candidate for the neutral N vacancy in AlN.

Following the one-electron linear-combination of atomic-orbital approximation, we estimate the isotropic part a and the anisotropic part b of the hf A tensor to be: $a \sim 179.3$ MHz and $b \sim 11.2$ MHz. These correspond to the spin density on the s and p orbitals of four Al neighbors of $\sim 18\%$ and $\sim 54\%$, respectively, or $\sim 72\%$ in total.

In summary, we have observed the EI-1 EPR spectrum in electron-irradiated AlN. The spectrum shows a clear hf structure due to the interaction with four nearest Al neighbors. Based on the good agreement in the hf parameters estimated from EPR and obtained from *ab initio* supercell calculations for V_N^0 , we suggest the EI-1 defect to be the best candidate for the neutral N vacancy in AlN. The high spin localization suggests that the defect is a deep center.

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²I. Gorczyca, A. Svane, and N. E. Christensen, Phys. Rev. B **60**, 8147 (1999).

- ⁴C. Stampfl and C. G. Van de Walle, Phys. Rev. B 65, 155212 (2002).
- ⁵K. Atobe *et al.*, Jpn. J. Appl. Phys., Part 1 **29**, 150 (1990).
- ⁶M. Honda et al., Jpn. J. Appl. Phys., Part 2 29, L652 (1990).
- ⁷P. M. Mason *et al.*, Phys. Rev. B **59**, 1937 (1999).
- ⁸S. M. Evans *et al.*, Appl. Phys. Lett. **88**, 062112 (2006).
- ⁹Á. Szabó et al., Appl. Phys. Lett. **96**, 192110 (2010).
- ¹⁰J. P. Perdew *et al.*, Phys. Rev. Lett. **77**, 3865 (1996).
- ¹¹P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
- ¹²G. Kresse and J. Hafner, Phys. Rev. B 49, 14251 (1994).
- ¹³P. E. Blöchl, C. J. Först, and J. Schimpl, Bull. Mater. Sci. 26, 33 (2003).

¹Y. Taniyasu, M. Kasu, and T. Makimoto, Nature (London) **441**, 325 (2006).

³A. Fara, F. Bernardini, and V. Fiorentini, J. Appl. Phys. 85, 2001 (1999).