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Silicon in AlN: shallow donor and DX behaviors

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In unintentionally Si-doped AlN bulk samples, an electron paramagnetic resonance (EPR) spectrum with characteristics of a shallow donor, previously assigned to the shallow Si donor, was observed at room temperature in darkness. Temperature dependent studies of the EPR sig-

nal showed that Si is a DX center in AlN. However, with the negatively charged DX⁻ state determined to be only ~78 meV below the neutral shallow donor state, Si should behave as a shallow dopant in AlN at normal device operating temperatures.

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1 Introduction Silicon (Si) and oxygen (O) are residual impurities in GaN, AlN and their alloys Al_xGa_{1-x}N. It is known that Si and O are effective-mass-like donors in GaN. Calculations [1-3] suggested that in AlN and Al_xGa_{1-x}N with Al content above a certain level, O undergoes a large lattice relaxation, forming a so-called deep DX state capturing a second electron to lower its energy. The process turns the shallow neutral charge state d⁰ to a deep negative charge state (2d⁰ → d⁺ + DX⁻) [1] and hence O behaves as a self-compensated center. For Si the properties are still under debate. Some calculations [1,2] suggested that similar to O, Si also forms DX state in AlN and Al_xGa_{1-x}N with high Al contents and cannot be used as a *n*-type dopant in the materials. On the contrary, other calculations [3] predicted Si to be a shallow donor for all values of *x*. Reported experimental data are also controversial. Some suggested DX behavior for Si [4,5]. The electron paramagnetic resonance (EPR) spectrum of the shallow Si donor has so far been detected only at low temperatures (below 60 K) under or after illumination [5,6]. This behavior was explained by the DX model of Si with the DX⁻ state lying at 320 meV below the conduction band minimum (CBM) [5] or by the carrier compensation of the shallow Si donor due to deep-level defects [6]. In more recent transport studies, high *n*-type conductivity was obtained in Si-doped AlN films and Si was proposed to be a shallow effective-mass-like donor [7-10]. In this work, we report our observation of the EPR signal of Si in unintentionally Si-doped AlN

bulk samples in darkness at room temperature. We will show from the temperature dependence of the EPR signal that Si is indeed a DX center in AlN but its DX⁻ state is located only ~78 meV below the shallow d⁰ level and Si should therefore behave as a shallow dopant at room temperature.

2 Experiment The AlN bulk samples were grown by physical vapor transport (PVT) using standard growth conditions and multiple resublimation of the source material prior to growth [11]. Different parts of the bulk crystals were grown on different facets forming domains (zonal structure) with different impurity incorporation cf. [12]. Secondary ion mass spectrometry (SIMS) measurements show that the concentration of Si is ~7×10¹⁷ cm⁻³ or slightly higher in unintentionally Si-doped samples and is in the SIMS background detection (<2×10¹⁶ cm⁻³) in nominal undoped samples. The concentration of carbon and O are ~2×10¹⁸ and ~4×10¹⁸ cm⁻³, respectively, in both undoped and unintentionally Si-doped AlN materials. EPR measurements were performed in an X-band (~9.5 GHz) Bruker E500 spectrometer. For illumination, a 200 W halogen lamp and appropriate optical filters were used.

3 Results and discussion Fig. 1 shows EPR spectra in undoped and unintentionally Si-doped AlN samples measured in darkness at room temperature for the magnetic field parallel to the *c*-axis (**B**||*c*). In nominal undoped AlN

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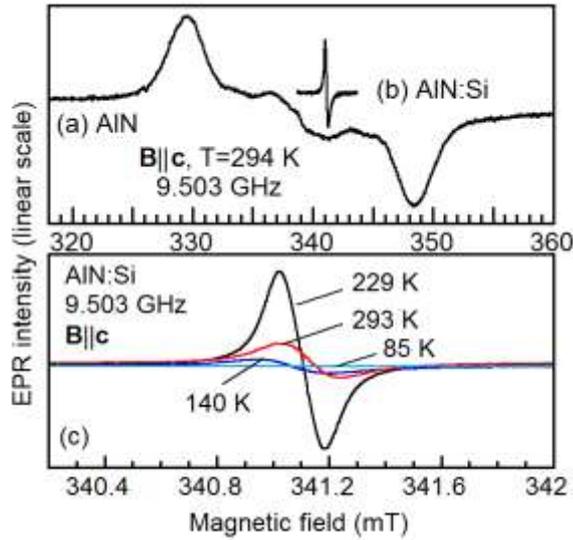


Figure 1 (color online) EPR spectra in (a) undoped and (b-c) unintentionally Si-doped AlN samples measured in darkness for $\mathbf{B}||c$ at different temperatures.

samples, the EPR spectrum of the neutral N vacancy (V_N^0) [13] was observed (Fig. 1a), whereas in unintentionally Si-doped samples, only a sharp line was detected (Fig. 1b). This line has an isotropic g -value of $g=1.9905\pm 0.0001$. From the g -value and the line width of the spectrum (less than 0.1 mT at low temperatures), it can be concluded that the spectrum in our Si-doped AlN has been previously reported in AlN films ($\sim 1.5 \mu\text{m}$ thick) grown on sapphire substrates ($g=1.9885$) [5] and in bulk AlN ($g=1.990$) [6].

When cooling down the sample in darkness, the signal was first increased, reaching its maximum at ~ 200 - 230 K and then gradually decreased to zero at ~ 85 K (Fig. 1c). From 80 K, we warmed up the sample in darkness and observed again the signal at ~ 95 K. As can be seen in the figure, the resonance position of the line shifted to low magnetic field with decreasing temperature, showing a temperature dependence of the g -value characteristic for shallow donor centers [14,15]. This supports the previous identification of the signal in Si-doped AlN samples to be related to the Si shallow donor [5,6].

Using a super high-Q cavity specially calibrated by Bruker for spin counting [16], we could determine the number of spins from the EPR intensity. From the weight of the sample and the density of AlN, the corresponding concentrations on the d^0 state can be determined (shown as open circles in Fig. 2). As can be seen in Fig. 2, the concentration is about constant ($\sim 6 \times 10^{15} \text{ cm}^{-3}$) at temperatures ~ 245 - 294 K. At lower temperature range, the concentration of the shallow state gradually decreases with decreasing temperature to below the detection limit of EPR (low 10^{14} cm^{-3}) at ~ 85 K. This temperature dependence indicates that the Fermi level E_F is not at the shallow donor state d^0 but is pinned at a slightly deeper level. This level should be close to the d^0 state so that the thermal excitation at 95 K can ef-

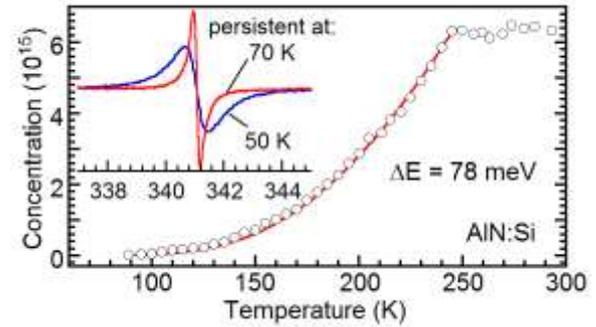


Figure 2 (color online) Temperature dependence of the number of spins (open circles) on the shallow state of the Si donor in AlN measured in darkness. The solid curve represents the fit using Eq (1). The inset shows the persistent signal measured at 50 K and 70 K after illumination at 40 K.

ficiently create a detectable population on the d^0 state.

Depending on the carrier compensation by the O DX-center, there are several possibilities: (i) Si is a shallow-effective-mass donor or a DX-center and E_F lies at the DX^- state of O and (ii) Si is a DX center and E_F lies at its DX^- state. In AlN, there is no valley-orbit splitting and hence the ionization energy of the shallow donor level is expected to be equal to the effective-mass-theory (EMT) value of a shallow donor which is ~ 60 meV [5] or ~ 65 meV [17] as calculated adapting the calculations in Ref. [18]. The shallow donor d^0 states of Si and O are expected to have similar ionization energy. In either case (i) or (ii), the decrease of the concentration of the shallow donor n_d with decreasing temperature in Fig. 2 can be described by the Boltzmann distribution of the shallow donor state of a DX center having four states: (i) a positive charge state with no electron present and zero energy (d^+ , $E^+=0$); (ii) two neutral charge states with a single electron occupation with different spin polarizations $M_S=\pm 1/2$ (d^0 , E_d); and (iii) a negative charge state with two electrons present (DX^- , E_{DX}). The temperature dependence of n_d is dependent on the energy separation between the shallow donor d^0 level and the Fermi level E_F , $\Delta E=E_d-E_F$

$$n_d(T) \propto N_d/[1+0.5\exp(\Delta E/k_B T)]. \quad (1)$$

Here N_d is the donor concentration at room temperature and E_F may lie at the DX^- state of either Si or O. In Eq (1), the terms related to the DX^- state of Si and/or O (in the case if E_F lies at the DX^- state of O), in the denominator with the form $0.5\exp[(E_d+E_F-E_{DX})/k_B T]$ can be neglected since $E_d+E_F-E_{DX}<0$. From the best fit of the temperature dependence of $n_d(T)$ using Eq (1) we obtained $\Delta E=78$ meV. Thus, in our Si-doped samples, the Fermi level lies at ~ 78 meV below the shallow donor level or ~ 0.14 eV below the CBM.

In accordance with Ref. [5], we also observed strong signal under illumination at low temperatures. At 40 K, the

1 signal is persistent after illumination (the corresponding
2 concentration is $\sim 8.5 \times 10^{17} \text{ cm}^{-3}$). With increasing the tem-
3 perature in darkness, the signal decreased and its line width
4 reduced from $\sim 0.5 \text{ mT}$ at 40-50 K to $\sim 0.1\text{-}0.15 \text{ mT}$ at $T > 70$
5 K (see the inset in Fig. 2). We believe that the broad signal
6 observed under illumination is mainly contributed from the
7 O shallow donor. [For O, the hyperfine (hf) interaction
8 with four ^{27}Al (nuclear spin $I=5/2$, nuclear g_n -value of
9 1.45601) neighbors is expected to give rise to a resonance
10 consisting of a larger number of unresolved hf lines with a
11 larger hf splitting than that of Si which has the hf interac-
12 tion with four nearest ^{14}N ($I=1$, $g_n=0.4037067$) neighbors.]

13 The temperature dependence of the EPR signal before
14 and after illumination support the second case, i.e., Si is a
15 DX center and E_F lies at its DX^- state. In equilibrium, due
16 to carrier compensation, this level was only partly populat-
17 ed whereas all O were in its DX^- state which lies deeper.
18 The shallow donor state can be activated by removing elec-
19 trons from its DX^- state. In the studied temperature range,
20 the electron removal by thermal energy can be efficient for
21 Si having its DX^- state lying only $\sim 0.14 \text{ eV}$ below the d^0
22 state, but not for O. As a result, only the signal of the Si
23 shallow donor was observed. Under illumination or after il-
24 lumination at $\sim 40 \text{ K}$, both the d^0 states of Si and O were
25 activated and their overlapping signals were detected. With
26 increasing temperature, electrons can overcome the energy
27 barrier between d^0 and DX^- states to relax back to lower-
28 lying DX^- levels, resulting in the decrease of the persistent
29 signal. At above 70 K , O is mostly in the DX^- state and the
30 persistent signal is mainly contributed from Si since the
31 donor activation is still possible for Si with its shallower
32 DX^- level. After illumination, the population on the d^0 and
33 DX^- states of Si increased. Therefore, thermal excitation at
34 $T < 85 \text{ K}$ could induce a larger population on the d^0 state
35 compared to that before illumination and the EPR signal
36 was observed (the concentration is $\sim 2 \times 10^{16} \text{ cm}^{-3}$ at $\sim 85 \text{ K}$).

37 The observation of the EPR signal of the Si shallow
38 donor in darkness at temperatures above $\sim 95 \text{ K}$ suggests
39 that the concentration of the isolated O DX center should
40 be considerably less than the total O concentration deter-
41 mined by SIMS. In AlN, O has been predicted to form
42 complexes such as the O-vacancy pair, $\text{O}_\text{N}-\text{V}_\text{Al}$ [19], or the
43 close O pair, $\text{O}_\text{N}-\text{O}_\text{N}$, a stable donor center [20]. The for-
44 mation of the $\text{O}_\text{N}-\text{O}_\text{N}$ pair should be possible in AlN crys-
45 tals grown by PVT at $\sim 2250 \text{ }^\circ\text{C}$ but may not occur in epi-
46 taxial AlN layers grown by metalorganic vapor phase epi-
47 taxy typically at $1100\text{-}1400 \text{ }^\circ\text{C}$. The formation of O-related
48 donor complexes may explain the lower level of carrier
49 compensation than expected in our samples.

50 The DX properties with a shallow level d^0 and DX^- at
51 $\sim 65 \text{ meV}$ and $\sim 0.14 \text{ eV}$, respectively, below the CBM may
52 explain the large variation of reported ionization energies
53 of the Si shallow donor in AlN in transport studies. De-
54 pending on the Si concentration and carrier compensation,
55 the Fermi level can be at the DX^- level of either Si or O.
56 The ionization energy obtained from the analysis of
57 transport data using the shallow donor model with one lev-

el system can be close to an average of the energies of the
 d^0 state ($\sim 65 \text{ meV}$) and the DX^- state of either Si (~ 0.14
 eV) or O depending on the level of carrier compensation
(e.g., $\sim 86 \text{ meV}$ [7], $\sim 180 \text{ meV}$ [8], $60\text{-}180 \text{ meV}$ [9] and
 $\sim 250 \text{ meV}$ [10]).

In summary, we have observed the EPR signal of the
shallow Si donor in darkness at temperatures above 95 K .
The temperature dependence of the EPR signal suggests
that Si is a DX center in AlN its DX^- state lying at ~ 78
 meV below the shallow donor d^0 state or $\sim 0.14 \text{ eV}$ below
the CBM. With such relatively small ionization energy, Si
should behave as a shallow dopant in AlN at normal device
operating temperatures.

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References

- [1] C.H. Park and D.J. Chadi, Phys. Rev. B **55**, 12995 (1997).
- [2] P. Boguslawski and J. Bernholc, Phys. Rev. B **56**, 9496 (1997).
- [3] C.G. Van de Walle, Phys. Rev. B **57**, R2033 (1998).
- [4] S. Skierbiszewski, T. Suski, M. Leszczynski, M. Shin, M. Skowronski, M.D. Bremser, and R.F. Davis, Appl. Phys. Lett. **74**, 3833 (1999).
- [5] R. Zeisel, M. W. Bayerl, S.T.B. Goennenwein, R. Dimitrov, O. Ambacher, M.S. Brandt, and M. Stutzmann, Phys. Rev. B **61**, R16283 (2000).
- [6] K. Irmscher, T. Schulz, M. Albrecht, C. Hartmann, J. Wollweber, and R. Fornari, Physica B **401-402**, 323 (2007).
- [7] Y. Taniyasu, M. Kasu, and N. Kobayashi, Appl. Phys. Lett. **81**, 1255 (2002).
- [8] M.L. Nakarmi, K.H. Kim, K. Zhu, J.Y. Lin, and H.X. Jiang, Appl. Phys. Lett. **85**, 3769 (2004).
- [9] T. Ive, O. Brandt, H. Kostial, K.J. Friedland, L. Däweritz, K.H. Ploog, Appl. Phys. Lett. **86**, 024106 (2005).
- [10] B. Borisov et al., Appl. Phys. Lett. **87**, 132106 (2005).
- [11] M. Bickermann, B.M. Epelbaum, O. Filip, P. Heimann, S. Nagata, A. Winnacker, Phys. Stat. Sol. (c) **7**, 21 (2010).
- [12] M. Bickermann, P. Heimann, B.M. Epelbaum, Phys. Stat. Sol. (c) **3**, 1902 (2006).
- [13] S.M. Evans, N.C. Giles, L.E. Halliburton, G.A. Slack, S.B. Schujman, and L.J. Schowalter, Appl. Phys. Lett. **88**, 062112 (2006).
- [14] D.J. Chadi, A.H. Clark, and R.D. Burnham, Phys. Rev. B **13**, 4466 (1976).
- [15] M.W. Bayerl, M.S. Brandt, T. Graf, O. Ambacher, J.A. Majewski, M. Stutzmann, D.J. As, and K. Lischka, Phys. Rev. B **63**, 165204 (2001).
- [16] P. Carl and P. Höfer, Bruker Report **159-160**, 17 (2008).
- [17] I.G. Ivanov, privat communication.
- [18] I.G. Ivanov, A. Stelmach, M. Kleverman, and E. Janzén, Phys. Rev. B. **73**, 045205 (2006).
- [19] T. Mattila and R.M. Nieminen, Phys. Rev. B **55**, 9571 (1997).
- [20] S.Petit, R. Jones, M.J. Shaw, P.R. Briddon, B. Hourahine, and T. Fruenheim, Phys. Rev. B **72**, 073205 (2005).