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Shallow donor and DX states of Si in AlN

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In unintentionally Si-doped AlN, the electron paramagnetic resonance (EPR) spectrum of the Si shallow donor ($g=1.9905$) was observed in darkness at room temperature. The temperature dependence of the EPR signal suggests that Si in AlN is a DX center with the DX^- state lying at ~ 78 meV below the neutral shallow donor state. With such relatively small thermal activation energy, Si is expected to behave as a shallow dopant in AlN at normal device operating temperatures. © 2011 American Institute of Physics. [doi:10.1063/1.3559914]

In AlN or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ with the aluminum (Al) content above a certain level, oxygen (O) is predicted to undergo a transition from a shallow to a deep center, the so-called DX state which can capture a second electron.¹⁻³ This leads to the formation of a negatively charged DX^- state and an ionized donor state d^+ : $2d^0 \rightarrow d^+ + DX^-$.

Silicon (Si) has so far been the only widely used n -type dopant in AlN and its alloys. However, its electronic structure in AlN is still not well understood. Several theoretical calculations^{1,2} predicted that Si on Al site in AlN and in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ with $x > 0.24$ or $x > 0.6$ has a stable DX state and cannot be a shallow dopant in this material. On the contrary, Van de Walle³ found that in wurtzite AlN Si remains a shallow-effective-mass donor. Reported experimental data on Si in AlN and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ are also controversial. Some transport studies suggested that when $x > 0.5$, Si undergoes a transition from the shallow donor to a localized DX state.⁴ The electron paramagnetic resonance (EPR) spectrum of the shallow Si donor has so far been observed only under illumination at low temperatures (below 60 K).^{5,6} EPR and photoconductivity studies⁵ suggested that Si in AlN has a stable DX state located at 320 meV below the conduction band minimum (CBM). However, in later transport studies, high n -type conductivity has been obtained in Si-doped $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and AlN and Si was suggested to be a shallow donor.⁷⁻¹⁰ The activation energy of Si was found to increase sharply with large Al contents and different values in the range of 60–250 meV were reported for AlN.⁷⁻¹⁰ Recently, EPR, thermal luminescence and electrical measurements⁶ of Si-doped AlN grown by physical vapor transport (PVT) suggested a model of the shallow Si donor compensated by acceptorlike electron traps within 1 eV below the CBM as an alternative to the assumption of Si DX -center formation.

In this letter, we present our EPR study of unintentionally Si-doped AlN bulk grown by PVT. The EPR spectrum of the shallow Si donor was observed in darkness at room temperature. We will show from the temperature dependence of the EPR signal that in AlN, Si behaves as a DX center as previously suggested⁵ but with the DX^- state lying only ~ 78 meV below the d^0 state.

The AlN bulk samples were grown by 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 (zonar structure) with different impurity incorporation, cf., Ref. 12. Such parts were separately prepared and are labeled undoped and unintentionally Si-doped, respectively, according to their impurity content. Secondary ion mass spectrometry (SIMS) measurements show that the concentration of Si is $7 \times 10^{17} \text{ cm}^{-3}$ or slightly higher in unintentionally Si-doped samples and is in the SIMS background detection ($< 2 \times 10^{16} \text{ cm}^{-3}$) in undoped samples. The concentration of carbon and O are $\sim 2 \times 10^{18} \text{ cm}^{-3}$ and $\sim 4 \times 10^{18} \text{ cm}^{-3}$, respectively, in both undoped and Si-doped materials. EPR measurements were performed on a Bruker E500 spectrometer. For illumination, a 200 W halogen lamp and appropriate optical filters were used.

In darkness at room temperature, only the signal previously identified to be related to either the neutral N vacancy (V_N^0) or the O on N site (O_N) (Ref. 13) was observed in undoped AlN samples, whereas in unintentionally Si-doped AlN samples, only a sharp EPR line (~ 0.1 – 0.2 mT in line width) was detected (Fig. 1). The g -value of this signal is isotropic ($g=1.9905 \pm 0.0001$ at 294 K). From the g -value and the line width, it can be concluded that the spectrum has been previously reported as related to the Si shallow donor in AlN films ($\sim 1.5 \mu\text{m}$ thick) grown on sapphire substrates ($g=1.9885$) (Ref. 5) and in bulk AlN ($g=1.990$).⁶ The spectrum in undoped samples¹³ was detected in Si-doped samples after implanting with Si in darkness. We believe that this spectrum is related to an intrinsic defect and not to O.

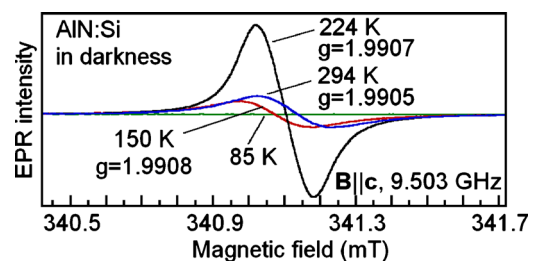


FIG. 1. (Color online) EPR spectra of the shallow Si donor in unintentionally Si-doped AlN measured in darkness for $B||c$ at different temperatures during cooling down the sample. The EPR signal is disappeared when cooling the sample to ~ 85 K in darkness. A small shift in the EPR line to lower magnetic fields is due to the temperature dependence of the g -value of the shallow donor.

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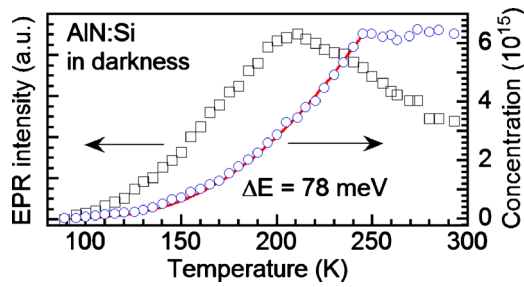


FIG. 2. (Color online) Temperature dependence of the EPR intensity (double integrals) of the shallow donor signal (open squares) in AlN measured in darkness with microwave power of 1 mW and the corresponding concentration on the shallow d^0 level (open circles) assuming a uniform doping in the sample. The solid curve represents the fits using Eq. (1).

Figure 1 shows EPR spectra measured at four different temperatures. As can be seen in the figure, the line was shifted to lower magnetic fields with decreasing temperature. A corresponding increase in the g -value from 1.9905 at 294 K to 1.9908 at 115 K was observed. It is known that electrons bound to shallow effective-mass donors and free electrons in the conduction band have roughly the same g -value¹⁴ which is dependent on the band gap and can be evaluated by the $k.p$ model.¹⁵ It has been shown in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ that the g -value of the shallow donor increases with increasing the band gap.¹⁶ The temperature dependence of the g -value in our case (i.e., the g -value increases with increasing the band gap caused by decreasing temperature) supports the previous identification of the EPR signal in Si-doped AlN as due to the Si shallow donor.^{5,6}

The temperature dependence of the signal intensity is plotted as open squares in Fig. 2 (left axis). The signal increased with decreasing temperature from ~ 294 to ~ 210 K and then gradually decreased and vanished at ~ 85 K. Warming up the sample in darkness to ~ 95 K, the signal appeared again. Using a superhigh-Q cavity (ER4119HS) specially calibrated by Bruker for spin counting,¹⁷ the corresponding absolute numbers of spins could be determined. The corresponding concentration of the shallow donor, n_d , determined from the obtained number of spins, the weight of the sample and the density of AlN, are plotted as open circles in Fig. 2 (right axis). The temperature dependence of the observed concentration is slightly different from that of the EPR intensity with $n_d(T) \sim 6 \times 10^{15} \text{ cm}^{-3}$ in the range of ~ 245 – 294 K and starts decreasing already at ~ 240 K (Fig. 2). This difference is due to the improvement of microwave coupling and hence the quality Q-factor of the cavity which enhances the EPR signal.

The observed temperature dependence of the concentration n_d in the d^0 state in Fig. 2 indicates that the Fermi level E_F is not at d^0 but is pinned at a deeper level. This level should be close to d^0 so that the thermal excitation at ~ 95 K can create a concentration detectable by EPR (in the low 10^{14} cm^{-3} ranges with assuming a uniform doping in the sample) on the d^0 state. There are several possibilities: (i) Si is a DX center and E_F lies at its lower-lying DX^- level (ii) Si is either a shallow donor or a DX center but due to carrier compensation E_F lies at the deeper DX^- state of O. In either case, the temperature dependence of the concentration n_d in Fig. 2 can be described by the Boltzmann distribution of the shallow donor level d^0 of a DX center having four states: a positive charge state with no electron present and zero ion-

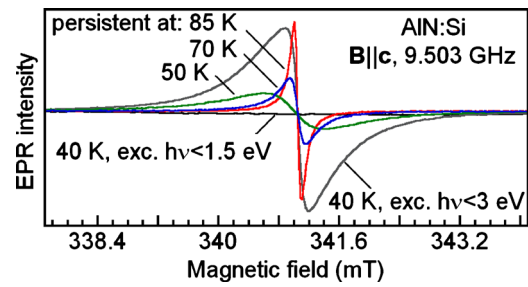


FIG. 3. (Color online) EPR spectra at 40 K under illumination with different photon energies and the persistent signals in darkness at different temperatures measured with the microwave power of 1 mW and a field modulation of 0.03 mT.

ization energy (d^+ , $E_+ = 0$ at the CBM); two neutral charge states with a single electron occupation with two different spin polarizations $M_S = \pm 1/2$ (d^0, E_d) and a negatively charged state with two electrons present (DX^-, E_{DX}). (Here the excited states of the shallow donor are neglected.) The decrease in the concentration of the d^0 state at low temperatures then can be described as¹⁸

$$n_d(T) \propto N_d \{1 + 0.5 \exp[(E_d - E_F)/k_B T]\}, \quad (1)$$

with N_d being the concentration of the shallow donor at ~ 245 – 294 K, k_B the Boltzmann constant, and T the temperature. Since E_d , E_{DX} , and E_F are negative and $|E_d| < |E_{DX}| \leq |E_F|$, we have $\Delta E = E_d - E_F > 0$ and $E_d + E_F - E_{DX} < 0$ for DX^- levels of either Si or O, the third term in the denominator of type $0.5 \exp[(E_d + E_F - E_{DX})/k_B T]$ can be neglected. The best fit gives the thermal activation energy $\Delta E = 78 \text{ meV}$. Since there is no valley-orbit splitting in AlN, the ionization energy of the shallow donor is expected to be equal to the effective-mass-theory value which was estimated to be $\sim 60 \text{ meV}$ (Ref. 5) or $\sim 65 \text{ meV}$ (Ref. 19) (adapting calculations in Ref. 20). Thus, in our Si-doped AlN samples Si behaves as a DX center with the Fermi level lying at $\sim 78 \text{ meV}$ below the shallow donor d^0 level or at $\sim 0.14 \text{ eV}$ below the CBM. Depending on the Si concentration and the level of carrier compensation by the O DX center, E_F may lie at the DX^- level of either Si or O.

We checked the effect of illumination at 40 K and observed no EPR signal when using light of photon energies $h\nu < 1.5 \text{ eV}$ (Fig. 3) in accordance with Ref. 5. With $h\nu < 1.8 \text{ eV}$, a line with the same g -value but broader ($\sim 0.5 \text{ mT}$ in line width) appeared. This line increased rapidly with increasing the photon energy and reached its maximum when $h\nu < 3 \text{ eV}$ (the signal corresponds to a concentration of $\sim 9 \times 10^{17} \text{ cm}^{-3}$) (Fig. 3). After illumination, the spectrum is persistent in darkness. Increasing temperature leads to a rapid decrease in the signal and its line width (from $\sim 0.5 \text{ mT}$ at 40–50 K to ~ 0.1 – 0.15 mT at $T > 70 \text{ K}$) (Fig. 3). We believe that the shallow O donor is the best candidate for the broad signal observed under or after illumination at low temperatures (40–50 K) since its the hyperfine (hf) interaction with four ^{27}Al (nuclear spin $I=5/2$, nuclear g_n -value of 1.456 01) neighbors is expected to give rise to a resonance consisting of a larger number of unresolved ^{27}Al hf lines with a larger ^{27}Al hf splitting than that of Si which has the hf interaction with four nearest ^{14}N ($I=1$, $g_n=0.403 706 7$) neighbors. The observation of the persistent broad and narrow signals indicates that the charge state associated with the EPR signals is different from that of the

ground state and there exists an energy barrier, E_B , between the states that helps to keep electrons from relaxing down to the ground state after illumination. This is typical for a DX center (see Ref. 5 for a typical scheme of energy levels). At $T > 70$ K, the broad signal, which we tentatively assign to the shallow O donor, is disappeared and the sharp line is mainly contributed from the Si shallow donor.

The temperature dependence of the EPR signal before and after illumination can be explained by the presence of two DX centers, Si and O, with the DX^- state of O lying deeper than that of Si. The Fermi level is at the DX^- state of Si which is only partly populated due to carrier compensation by the deeper DX^- state of O. Removing one electron from the DX^- state to the d^+ state will automatically turn the center to the shallow d^0 state which can be detected by EPR. Under or after illumination at low temperatures, the signals of both Si and O shallow donors were detected. The broader line width of the signal reflects the major contribution from the O shallow donor due to its higher concentration. After illumination, the population on the d^0 state of Si or O is mainly governed by three processes: (i) electron removal from the d^0 state to the DX^- state via the energy barrier E_B , (ii) ionization of the donor with removing electrons from the d^0 state to the CBM (d^+), and (iii) thermal excitation of electrons from the DX^- state to the d^+ state, activating the neutral d^0 state. Since the persistent signal already significantly decreases at ~ 50 K (see Fig. 3) or could not be detected at ~ 60 K,⁵ the energy barrier E_B should be small for both Si and O and process (i) is dominating in this low temperature range. The ionization energy E_d of Si and O are expected to be similar (the difference due to the chemical shift is expected to be small as shown in GaN with $E_d \sim 30$ meV for Si and $E_d \sim 33$ meV for O)²¹ and hence the donor ionization process (ii) will be similarly efficient for both centers. However, the donor activation process (iii) will be more efficient for Si with a shallower DX^- state (~ 0.14 eV below the CBM) than for O with a deeper DX^- state. Therefore, with increasing temperature the concentration on the d^0 state decreases faster for O than for Si and so does the corresponding contribution to the persistent signal, resulting in the reduction in the line width (Fig. 3). After illumination, the DX^- state of Si became fully occupied and hence thermal excitation at $T < 85$ K can result in a larger concentration in the d^0 level ($\sim 2 \times 10^{16}$ cm⁻³ at ~ 85 K) compared to that before illumination (not detectable by EPR). During the donor ionization and activation process, electrons being excited to the conduction band can also recombine to the deeper defect levels, which are not fully occupied after illumination, leading to the reduction in the population on the Si levels. Therefore, the signal decreased with increasing temperature and at $T > 130$ K, the system returns to the situation before illumination with a partly populated DX^- state.

Our results suggest that the concentration of the isolated O DX center in our Si-doped samples should be considerably less than the total O concentration of $\sim 4 \times 10^{18}$ cm⁻³ as determined by SIMS. The formation of O-related vacancy complexes, such as the O–Al vacancy pair (O_N-V_{Al}), in as-grown material can be expected.²² The close O pair (O_N-O_N) has been predicted to be a donor and the most

stable complex in AlN.²³ The formation of the O_N-O_N pair should be possible in samples grown by PVT at ~ 2250 °C but may not occur in epitaxial layers grown by metalorganic vapor phase epitaxy typically at 1100–1400 °C. The formation of O-related complexes may explain the lower level of carrier compensation by the O DX center than expected in our samples.

The Si DX center with the population of its DX^- level strongly dependent on the carrier compensation by the O DX center may explain the variation in the reported ionization energy of the shallow Si donor in AlN. In transport studies of Si-doped AlN,^{7–10} the analysis using the shallow donor model with one energy level cannot describe correctly the energy levels of the Si DX system, especially in the presence of another deeper O DX center with an unknown level of carrier compensation. Depending on the Si concentration and the level of carrier compensation, the obtained ionization energy in transport studies are expected to be sample dependent and close to an average of energies of the d^0 state (~ 65 meV) and the DX^- state of either Si (~ 0.14 eV) or O, e.g., ~ 86 meV as determined from an average of two slopes of the temperature dependence of the electron concentration,⁷ ~ 180 meV,⁸ ~ 60 – 180 meV,⁹ or ~ 250 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 in darkness and the persistent signal after illumination suggest that Si is a DX center with the DX^- state lying at ~ 78 meV below the shallow donor d^0 state or ~ 0.14 eV below the CBM. With such relatively small thermal activation energy, Si is expected to behave as a shallow dopant in AlN at normal device operating temperatures.

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