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 $\sim 78$ 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 $d^+$.4,2 $2d^-\rightarrow d^++DX^-$. 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 calculations5,6 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 Walle7 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.5,7–10 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 suggested4 but with the $DX^-$ state lying only $\sim 78$ meV below the $d^+$ state.

The AlN bulk samples were grown by PVT using standard growth conditions and multiple sublimation 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., Ref. 12. Such parts were separately prepared and were 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 $7 \times 10^{17}$ cm$^{-3}$ or slightly higher in unintentionally Si-doped samples and is in the SIMS background detection ($< 2 \times 10^{16}$ cm$^{-3}$) in undoped samples. The concentration of carbon and O are $\sim 2 \times 10^{18}$ cm$^{-3}$ and $\sim 4 \times 10^{18}$ 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 ($V_d^0$) or the O on N site ($O_d^+$) (Ref. 13) was observed in undoped AlN samples, whereas in unintentionally Si-doped AlN samples, only a sharp EPR line ($\sim 0.1–0.2$ 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 ($\sim 1.5$ µm thick) grown on sapphire substrates ($g=1.9885$) (Ref. 5) and in bulk AlN ($g=1.990$).9 The spectrum in undoped samples13 was detected in Si-doped samples after implantation 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 $\sim 85$ 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.
The corresponding concentration of the shallow donor, $n_d$, 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-value which is dependent on the band gap and can be evaluated by the $k.p$ model. It has been shown in Al$_x$Ga$_{1-x}$N that the g-value of the shallow donor increases with increasing the band gap. The temperature dependence of the g-value in our case supports the previous identification of the EPR signal in Si-doped AlN as due to the Si shallow donor.

The temperature dependence of the signal intensity is plotted as open squares in Fig. 2 (left axis). The signal increased with decreasing temperature from $\sim$294 to $\sim$210 K and then gradually decreased and vanished at $\sim$85 K. Warming up the sample in darkness to $\sim$95 K, the signal appeared again. Using a superhigh-Q cavity (ER4119HS) specially calibrated by Bruker for spin counting, 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 $\sim$245–294 K and starts decreasing already at $\sim$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 $\sim$95 K can create a concentration detectable by EPR (in the low $10^{14} \text{ cm}^{-3}$ 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 ionization energy ($d^+$, $E_{d^+}$=0 at the CBM); two neutral charge states with a single electron occupation with two different spin polarizations $M_{S^\pm}$ = $\pm 1/2$ ($d^0$, $E_{d^0}$) 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 as

$$n_d(T) \sim N_d/(1 + 0.5 \exp[(E_{d^0} - E_F)/k_BT]),$$

with $N_d$ being the concentration of the shallow donor at $\sim$245–294 K, $k_B$ the Boltzmann constant, and T the temperature. Since $E_{d^0}$, $E_{DX^-}$, and $E_F$ are negative and $|E_{d^0}| < |E_{DX^-}| \leq |E_F|$, we have $\Delta E = E_{d^0} - E_F > 0$ and $E_d + E_F - E_{DX^-} < 0$ for DX$^-$ levels of either Si or O, the third term in the denominator of type $0.5 \exp((E_d + E_F - E_{DX^-})/k_BT)$ 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 meV (Ref. 5) or $\sim$65 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 meV below the shallow donor $d^0$ level or at $\sim$0.14 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 $h\nu < 1.5$ eV (Fig. 3) in accordance with Ref. 5. With $h\nu < 1.8$ eV, a line with the same g-value but broader ($\sim$0.5 mT in line width) appeared. This line increased rapidly with increasing the photon energy and reached its maximum when $h\nu < 3$ 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 mT at 40–50 K to $\sim$0.1–0.15 mT at T > 70 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

![Figure 2](image1.png)  
**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 3](image2.png)  
**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.
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 $d^0$ 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 $d^0$ state, activating the neutral $d^0$ state. Since the persistent signal already significantly decreases at $\sim 50$ K (see Fig. 3) or could not be detected at $\sim 60$ K, 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 $E_{id}$ 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 $E_{id} \sim 30$ meV for Si and $E_{id} \sim 33$ meV for O) 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 ($\sim 0.14$ 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 ($\sim 2 \times 10^{14}$ cm$^{-3}$ at $\sim 85$ 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. The close O pair (O$_N$–O$_N$) has been predicted to be a donor and the most stable complex in AlN. The formation of the O$_N$–O$_N$ pair should be possible in samples grown by PVT at $\sim 2250$ °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, 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 ($\sim 65$ meV) and the $DX^-$ state of either Si ($\sim 0.14$ eV) or O, e.g., $\sim 86$ meV as determined from an average of two slopes of the temperature dependence of the electron concentration.$^7$ $\sim 180$ meV$^8$ $\sim 60–180$ meV$^9$, or $\sim 250$ meV.$^{10}$

In summary, we have observed the EPR signal of the shallow Si donor in dark 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 $\sim 78$ meV below the shallow donor $d^0$ state or $\sim 0.14$ 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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19. I. G. Ivanov, private communication (June 2010).