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Influence of silicon doping on vacancies and optical properties of Al$_x$Ga$_{1-x}$N thin films

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The authors have used positron annihilation spectroscopy and photoluminescence measurements to study the influence of silicon doping on vacancy formation in AlGaN:Si structures. The results show a correlation between the Doppler broadening measurements and the intensity from 510 nm photoluminescence transition. The reduction in the $W$ parameter when the [Si]/[Al+Ga] fraction in the gas phase is above $3 \times 10^{-4}$ indicates that the positrons annihilate in an environment where less Ga 3$d$ electrons are present, i.e., they are trapped in group-III vacancies. The observation of vacancies at these silicon concentrations coincides with the onset of the photoluminescence transition at 510 nm. © 2007 American Institute of Physics. [DOI: 10.1063/1.2721132]

UV devices based on AlGaN alloys have gained a lot of interest in recent years and are already commercially available. 1 AlGaN systems are especially suitable for these applications since they cover wavelengths from 200 to 364 nm. For almost any semiconductor system, one of the crucial requirements is the possibility to produce and control the doping of the layers. Previously, $n$-type doping of Al$_x$Ga$_{1-x}$N was considered a problem since the carrier concentration decreased with increasing Al mole fraction $x$. 2 Progress in this field has been made by several groups and low resistivity Al$_x$Ga$_{1-x}$N layers as well as $n$-type doping of AlN have been reported. 3–6

Silicon is the most commonly used element of $n$-type doping of AlGaN structures. Hence, the reason for its electrical deactivation with increasing Al mole fraction has been the focus of some debate lately. Calculations by Van de Walle et al. showed that the Al vacancy can act as a compensator in its triply ionized state, with the Fermi level close to the conduction band in AlN. 7 Furthermore, since the band gap increases with increasing Al content, the formation energy for the group-III vacancy decreases. Wagener et al. reported on the deepening of the Si level with increasing Al content ($x=0.2–0.5$), as well as on the presence of two levels in the band gap thought to be responsible for the compensation. 8 Keller et al. proposed that observed PL transition in the 510–550 nm range is due to the group-III vacancy. 9

In this letter, we confirm the correlation between the vacancy concentration in the group-III sublattice and the photoluminescence (PL) transition in the 510–550 nm range by combining positron annihilation spectroscopy (PAS) with photoluminescence measurements. Furthermore, we have investigated the effect of silicon doping on vacancy formation in AlGaN layers. We observe an increase both in the PL intensity and the vacancy concentration when the [Si]/[Al+Ga] fraction in the gas phase increases above $3 \times 10^{-4}$.

For these experiments, Al$_{0.63}$Ga$_{0.37}$N:Si films of different doping levels were grown by metal-organic chemical vapor deposition. The aluminum and gallium sources were TMAl and TMGa, and the nitrogen source NH$_3$. The substrates used were 4H-SiC, upon which buffer layers of 150 nm of AlN followed by 460 nm of unintentionally doped Al$_{0.63}$Ga$_{0.37}$N were deposited. The doped layers in question were 300 nm thick, with a dislocation density of $5 \times 10^9$ cm$^{-2}$. The [Si]/[Al+Ga] ratio was varied from $3.5 \times 10^{-3}$ to $6 \times 10^{-4}$ over the five samples by modifying the Si$_2$H$_6$ precursor flow. The dislocation density did not depend on the [Si]/[Al+Ga] ratio.

Hall measurements performed on the samples at room temperature showed a linear increase in carrier concentration with increasing Si content up to a [Si]/[Al+Ga] ratio of $3 \times 10^{-4}$, while the mobility decreased linearly over the same sample range. Above this level of Si content, the carrier concentration decreased slightly while the mobility decreased at a sharper rate of decline. Further details on the electrical characteristics have been published in Ref. 10.

In order to determine the vacancy content in the thin layers, we used a variable energy positron beam. After implantation the positrons thermalize rapidly and diffuse in the lattice until they annihilate with electrons. Neutral and negative vacancy-type defects in the lattice act as positron traps. When a positron is trapped by a vacancy, the positron-electron momentum distribution narrows and the momentum of the annihilating positron-electron pair can be detected as a reduction in Doppler broadening of the 511 keV annihilation line. For the description of shape of the broadened annihilation line, we used the conventional $S$ and $W$ parameters. 11 The $S$ parameter is the fraction of annihilation events in the central part of the annihilation peak and thus describes annihilation mainly with low momentum valence electrons. The $W$ parameter is calculated from the wings of the annihilation peak and describes annihilation mainly with high momentum core electrons. Generally an increase (decrease) in the $S(W)$ parameter indicates the presence of vacancy-type defects. In
As can be seen from the \( W \) parameter in Fig. 1, the samples are divided into two groups when comparing the \( W \) parameters in the peak region, where the annihilation signal mainly comes from the silicon doped layer. The differences between the samples can be easily observed in Fig. 2, where the \( W \) parameter in the AlGaN:Si layer is presented as a function of the [Si]/[Al+Ga] fraction in the gas phase. A change in the \( W \) parameter to lower values can be seen when the silicon fraction reaches \( 3 \times 10^{-4} \) indicating that the annihilation environment of the positrons changes. This fraction corresponds to a free electron concentration of \( 7.5 \times 10^{18} \text{ cm}^{-3} \).

The main contributors to the momentum intensity in the \( W \) parameter region are Ga 3d electrons. Thus, the reduction in the \( W \) parameter when the silicon doping in AlGaN reaches approximately \( 3 \times 10^{-4} \) is due to a reduction in the Ga content in the environment of the annihilating electron positron pair. This means that the positron is trapped by a defect surrounded by nitrogen atoms, i.e., a group-III vacancy. An estimate for the vacancy concentration can be obtained when assuming that the \( W \) parameter for the group-III vacancy in AlGaN is similar to that in GaN. The deduced vacancy concentration in the samples with the silicon fraction of \( 3 \times 10^{-4} \) or higher is thus in the \( 10^{17}–10^{19} \text{ cm}^{-3} \) range.

The PL spectra of the AlGaN:Si films were characterized by bright band edge related luminescence at 254 nm. Two characteristic deep level transitions were also observed in all samples, one centered at 410 nm and a second one at 510 nm. A detailed investigation of the impact of the growth conditions on the PL properties previously performed in the same reactor and combined with secondary-ion-mass spectroscopy analysis indicated that the relative intensity of the 410 nm level increased with the impurity concentration in the films, in particular, oxygen. In contrast, the 510 nm level did not show any correlation with the residual impurities in the films and was tentatively associated with a native defect, the group-III vacancy, in Ref. 9. The relative PL intensity between this transition and the band edge emission as a function of Si content is shown in the inset of Fig. 3.

The comparison between the trends observed in PL and in the positron annihilation experiments, showing a direct correlation between the luminescence peak centered around 510 nm and the \( W \) parameter confirms its association with the group-III vacancy or a complex involving the group-III vacancy or a complex involving the group-III vacancy.

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The comparison between the trends observed in PL and in the positron annihilation experiments, showing a direct correlation between the luminescence peak centered around 510 nm and the \( W \) parameter confirms its association with the group-III vacancy or a complex involving the group-III vacancy. Since the 410 nm level follows the same trend with increasing Si doping, this level is probably also associated with a vacancy in the group-III sublattice. A likely candidate for a group-III vacancy complex is \( V_{\text{Ga}}-\text{O}_{\text{N}} \), which is typical in GaN (Refs. 12–14) and has also been predicted theoretically.
We have combined positron annihilation spectroscopy and photoluminescence measurements to study the influence of silicon doping on vacancy formation in AlGaN:Si layers. A clear correlation is found between silicon concentration, PAS Doppler parameters $S$ and $W$, and observed defect transitions in the PL measurements. We conclude that the vacancies in the group-III sublattice are responsible for the observed PL transitions at 510 nm. The vacancies appear when the [Si]/[Al+Ga] ratio in the gas phase is above $3 \times 10^{-4}$.

![PL spectra of an AlGaN:Si film with a [Si]/[Al+Ga] ratio of 1.5$ \times 10^{-4}$. Inset: relative PL intensity as a function of the Si fraction in the layer.](image)

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