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**LETTER TO THE EDITOR**

# Defects in GaN films studied by positron annihilation spectroscopy

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**Abstract**

The annealing of n-type thin GaN films grown by metal–organic chemical vapour deposition in vacuum has been studied by beam-based positron annihilation spectroscopy. The results are consistent with a model in which Ga vacancies ($V_{Ga}$) exist alongside dislocations and are stable up to 900 °C. It is suggested that dislocations are shallow positron traps. Upon annealing at $\leqslant$500 °C the decrease of dislocation density increases the effective positron diffusion length ($L_{+eff}$) and the probability of trapping at $V_{Ga}$. While $L_{+eff}$ continues to change, the trapping of positrons at $V_{Ga}$ is saturated upon annealing above 500 °C. The formation of N vacancies near the surface at high temperatures is considered to introduce a potential that retards positron back-diffusion. At 900 °C dissociation of GaN at a rate of $\sim$5 nm $s^{-1}$ is observed. Oxygen clusters, stable up to 900 °C, appear to exist near the interface between the GaN film and the sapphire substrate.

## 1. Introduction

GaN is a very promising semiconductor material for optoelectronic and high-temperature electronic device applications. It is imperative that the nature of the defects in GaN and related materials, and the mechanisms for their formation and evolution, should be understood clearly so that the full potential of GaN and its alloys can be completely realized in device structures [1–3].

Positron annihilation spectroscopy (PAS) with a slow-positron beam is an efficient tool for the investigation of open-volume defects such as vacancies in semiconductors [4]. The implanted monoenergetic positrons can readily become trapped at open-volume defects as a result of the missing positive-ion core at these defects. The trapping gives rise to a narrowing of the momentum distribution of the positron–electron pair and thus also in the annihilation gamma energy spectrum. The latter is characterized by a higher $S$-parameter (or lower $W$-parameter) compared with the positron annihilation in defect-free lattice sites [4]. Here $S$ ($W$)

  

is defined as the ratio of the central (wing) area to the total area under the spectrum. The most probable point defects in GaN are believed to be N vacancies ($V_N$) in p-type GaN and Ga vacancies ($V_{Ga}$) in n-type GaN [5]. Whereas positively charged $V_N$ do not readily trap positrons, $V_{Ga}$ can be observed by PAS because they are usually negatively charged [6–8].

Open-volume defects are deep positron traps. However, shallow positron traps, such as negative ions and dislocations, also exist in semiconductors [9, 10]. Previous slow-positron studies of GaN films demonstrated that the effect of shallow traps could be clearly seen up to 500 K [6]. In this letter we investigate the defect structure of GaN films grown by metal–organic chemical vapour deposition (MOCVD) by studying the annealing behaviour from 150 to 900 °C.

## 2. Experimental procedure

The GaN samples were grown on (0001)-oriented sapphire by MOCVD at the University of Bath. The growth pressure was 200 mbar. Trimethyl gallium (TMG) and $NH_3$ were employed as precursors and $H_2$ as the gas carrier. A ∼20 nm thick nucleation layer was initially deposited on the substrate at low temperature. 400 nm undoped GaN was then grown, followed by 2 $\mu$m Si-doped n-type GaN at high temperature. The carrier density and Hall mobility of the as-grown sample were $2.2 \times 10^{17}$ cm$^{-3}$ and 390 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The samples were annealed for 2 min at temperatures in the range from 150 to 900 °C with an electron beam heater in a vacuum of $\sim 5 \times 10^{-5}$ Pa. Slow-positron measurements were carried out at room temperature for the as-grown sample and after every annealing step. In addition, a 3 $\mu$m thick lightly Mg-doped high-resistivity GaN film grown by MOCVD on a sapphire substrate was measured as a comparison.

Single-detector Doppler-broadening spectroscopy was performed using a magnetic transport positron beam system [11].

## 3. Results and discussion

Figure 1 shows the results of the slow-positron measurements. The incident positron energy $E$ (keV) corresponds to a mean probed depth of $\sim 6.7E^{1.6}$ nm. The measured $S$ can be expressed as a combination of different characteristic $S$ values at different positron annihilation sites. If we use $S_s$, $S_b$, $S_i$ and $S_{sub}$ to denote $S$ for positrons annihilated at the surface, in bulk GaN, in the interface region between GaN and sapphire and in the sapphire substrate, respectively, then the measured $S$ is

$$S = f_s S_s + f_b S_b + f_i S_i + f_{sub} S_{sub}, \tag{1}$$

where $f_s$, $f_b$, $f_i$ and $f_{sub}$ are the corresponding fractions of implanted positrons annihilated at the different sites at each $E$, respectively. At the lowest incident positron energy, 0.5 keV, it is assumed that essentially all the positrons are annihilated at the surface, and we therefore take the measured $S$ at 0.5 keV as $S_s$ in this study. When $E$ is increased to a value in the range from ∼10 to ∼18 keV, almost all the positrons are annihilated in bulk GaN. By implanting positrons from the sapphire side, $S_{sub}$ is obtained. $S_i$ cannot be obtained directly from the measurements. It is found that a good fit to the data cannot be achieved by the code VEPFIT [12] without incorporating a very low $S$ (∼0.330) in the first ∼300 nm region above the sapphire.

It has been demonstrated that the defects seen by positrons in GaN are $V_{Ga}$ [6–8]. There are fewer $V_{Ga}$ in Mg-doped GaN than in n-type GaN [7, 8]. The existence of $V_{Ga}$ can be confirmed if the measured $S$ values are larger than those of Mg-doped GaN, which is the case here (figure 1).

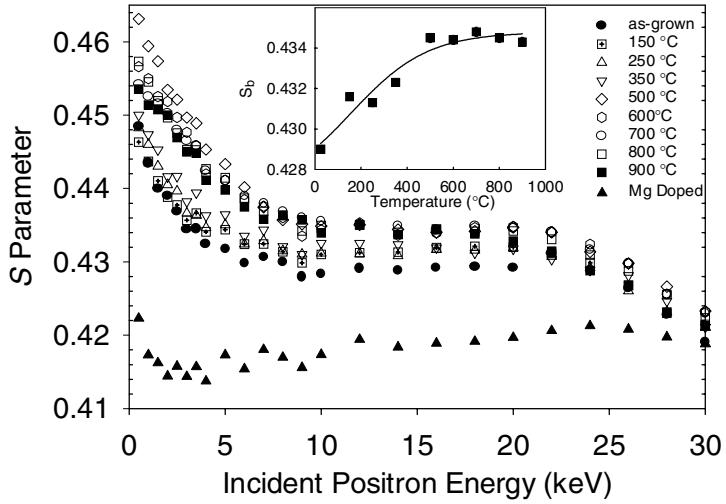


**Figure 1.** *S*-parameter versus incident positron energy for as-grown and annealed samples. A lightly Mg-doped sample is used as a comparison. The change of $S_b$ with annealing temperature is shown in the inset, where the solid curve is a sigmoidal fit.

It is interesting to note that $S$ increases slightly as $E$ increases from 9 to 20 keV for the as-grown sample. The increase is believed to be real because the error bars are smaller than the size of the data points in figure 1. This suggests that the $V_{Ga}$ concentration increases with depth. It should be noted that there are still some $V_{Ga}$ in the lightly Mg-doped sample because the formation energy of $V_{Ga}$, which is the function of Fermi level, is not high enough to block completely the formation of $V_{Ga}$ [8]. Hence, the increase of $V_{Ga}$ with depth can also be seen in our lightly Mg-doped GaN. In GaN, dislocations originate from the faulted regions located within the nucleation layer [13]. The dislocation density is very high within the first ∼400 nm from the substrate, and with the further growth of GaN it decreases towards the surface [14]. Therefore, the change of $V_{Ga}$ concentration is apparently correlated with that of dislocation density. A scanning capacitance microscopy study has indicated that there are negative charges near the dislocations [15], and these can result from $V_{Ga}$. In summary, $V_{Ga}$ appear to prefer to reside alongside dislocations.

After annealing $S_b$ increases until it becomes nearly constant at temperatures higher than 500 °C. The inset in figure 1 shows this change, where $S_b$ is taken as the average of the $S$ values measured in the positron energy range from 9 to 20 keV for the as-grown sample and those annealed below 500 °C, and the values on the flat part of the curve for the samples annealed at $\geqslant$500 °C. It is well known that by plotting $S$ versus $W$ one can determine whether or not a defect type remains unchanged under external influence [4]. It is clear from figure 2 that all the data fall on the same line, suggesting that the defects seen by positrons are $V_{Ga}$ in all the annealed samples.

It is tempting to attribute the increase of $S_b$ with annealing temperature to an increase in vacancy concentration. However, because the trapping rate of positrons is proportional to vacancy concentration, the effective positron diffusion length, $L_{+eff}$, will decrease when the vacancy concentration increases [4]. By using

$$f_s(E) = \int_0^\infty P(z) \exp(-z/L_{+eff})\, \mathrm{d}z, \tag{2}$$

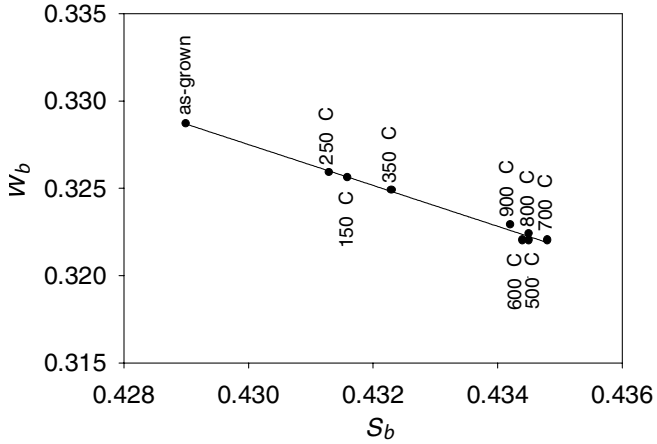


**Figure 2.** $W_b$ versus $S_b$ for the as-grown sample and annealed GaN from 150 to 900 °C.

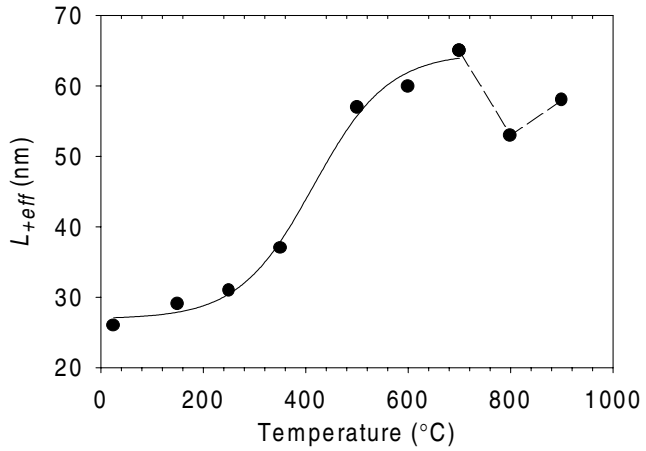


**Figure 3.** The change of effective positron diffusion length in as-grown and annealed GaN. The solid curve is a sigmoidal fit. The dashed line is used to guide the eye.

where $P(z)$ is the normalized positron implantation profile along the depth, $z$, at a positron implantation energy $E$, $L_{+eff}$ can be obtained by measuring $f_s$. Although the defect distribution is not uniform in the GaN film, as discussed before, the variation with depth of the PAS response is small. This is clear by looking, between ∼10 and ∼20 keV, at the small slopes for the as-grown sample and those annealed below 500 °C, and the nearly constant $S$ for those annealed above 500 °C (figure 1). Therefore, it is assumed that such a defect distribution is sufficiently homogeneous over the positron diffusion length in GaN to validate the use of equation (2) in our analysis. For each $E$ lower than ∼10 keV, $f_s$ can be calculated using equation (1) with $f_i = 0$, $f_{sub} = 0$ and the $S_b$ values illustrated in the inset of figure 1 (the real $S_b$ for the regions probed by positrons of energies lower than ∼10 keV may be slightly, but unimportantly, different). Figure 3 shows $L_{+eff}$ from the as-grown and annealed data by fitting $f_s$ versus $E$ with equation (2). It is evident that $L_{+eff}$ increases from ∼30 to ∼60 nm after the annealing at and above 700 °C. Hence, the increase of $S_b$ cannot be considered to be due to an increase of vacancy concentration.

The present results are therefore interpreted as follows. A fraction of the positrons detrapping from shallow traps can travel further, leading to the increase of $L_{+eff}$, and others can be trapped by $V_{Ga}$, leading to the increase of $S$. Given that shallow positron traps in GaN films have been seen up to 500 K [6], it is naturally believed that they play an important role in the present measurements at 300 K. It has been demonstrated that negative ions trap positrons only efficiently at temperatures below 200 K [16]. Therefore, although Saarinen *et al* surmised that negative ions acted as shallow traps at temperatures up to 500 K [6], we consider that dislocations are actually the main shallow traps in the present measurements; they have been observed to act as shallow traps in other semiconductor materials [10]. There is expected to be a high density of inherent dislocations in GaN.

As mentioned above, the total dislocation density decreases from the interface to the surface in GaN. In the region near the interface, most of the dislocations are not directed towards the surface along (0001), in contrast to those in the shallower region [17]. The higher density and randomness enable easier dislocation interaction in the deeper region, and thus the annealing of dislocations in the deeper region is efficient, even at temperatures $\leqslant$350 °C, which leads to the obvious increase in $S_b$ (inset, figure 1). However, the increase in $L_{+eff}$, which characterize the shallower region ($E$ lower than $\sim$10 keV), is very small (figure 3), resulting from the insignificant annealing of dislocations in the shallower region. When the temperature is increased to 500 °C, the annealing of dislocations becomes significant even in the shallower region. Therefore, an obvious increase in $L_{+eff}$ is observed (figure 3). Meanwhile, positron trapping in $V_{Ga}$ becomes nearly saturated, so the change in $S_b$ is small (inset, figure 1).

It can be seen that $S_b$ is approximately constant between 500 and 900 °C (inset, figure 1). This is in contrast to the change of $L_{+eff}$ (figure 3). The latter observation indicates that the dislocation density continues decreasing in this temperature range, consistent with XTEM measurements of the annealing of GaN between 600 and 800 °C [18]. After the samples are annealed above 500 °C, the associated increase in the number of positrons which can be trapped by $V_{Ga}$ does not increase $S_b$. This implies that the trapping at $V_{Ga}$ has been saturated.

We also notice that when the sample is annealed at >700 °C, $L_{+eff}$ decreases (figure 3). It is supposed that there are many N vacancies produced at the surface at 800 °C because this temperature is very near the dissociation temperature, 850 °C, of GaN in the vacuum [19]. These N vacancies can make the GaN more n-type owing to their donor nature. This results in a band bending near the surface, forming a potential that retards positron back-diffusion to the surface and the apparent decrease in $L_{+eff}$. Above 800 °C, changes are attributed to the dissociation of GaN.

Comparing the $S$-curve of 900 °C to those measured for lower temperatures, the energy denoting the interface between GaN and sapphire drops from 22 to 18 keV (figure 1). Using the code VEPFIT, the depth of the interface between GaN and sapphire is found to be at $\sim$1800 nm after the annealing at 900 °C. This corresponds to a dissociation rate of $\sim$5 nm $s^{-1}$, which is somewhat larger than the value of 1.2 nm $s^{-1}$ obtained by extrapolating the data of Grandjean *et al* [20]. This difference is probably due to the fact that in our system, which does not employ a rapid thermal process, efficient dissociation has happened before 900 °C.

Finally, we return to the very low $S$ in the interface region, as derived from the fitting program. Such a low $S$ can be explained by the presence of many oxygen clusters in that region. During the growth of GaN at high temperature, oxygen can diffuse from sapphire to the interface region, as has been indicated by SIMS measurements [21]. These oxygen atoms can easily form clusters because there are many defects such as voids that can act as the nucleation centres in the interface region. Oxygen clusters reduce $S$ to a value smaller than that for defect-free semiconductors [22]. Moreover, the present results suggest that these oxygen clusters are stable up to 900 °C because the low $S$ exists in all the samples. It should also be

noted that an electrical field probably exists near the interface, which can enhance positron diffusion to oxygen clusters or to sapphire and result in a smaller $S$.

## 4. Conclusions

The results presented in this letter suggest that $V_{Ga}$ exist alongside dislocations in GaN films and are stable up to 900 °C. Dislocations are believed to behave as shallow positron traps. The decrease of dislocation density increases the positron effective diffusion length and $S$-parameter for annealing at $\leqslant$500 °C. Above 500 °C, the trapping of positrons at $V_{Ga}$ is saturated and $S$ becomes constant, while $L_{+eff}$ continues to change. The near-surface formation of $V_N$ at high temperature can introduce a potential that retards positron back-diffusion. The dissociation rate of GaN at 900 °C is estimated to be $\sim$5 nm $s^{-1}$. In addition, the results are consistent with the presence of oxygen clusters in the $\sim$300 nm region near the interface, which are stable up to 900 °C

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