Tuomisto, Filip; Karjalainen, Antti; Prozheeva, Vera; Makkonen, Ilja; Wagner, Gunter; Baldini, Michele

Ga vacancies and electrical compensation in β-Ga$_2$O$_3$ thin films studied with positron annihilation spectroscopy

Published in:
Oxide-Based Materials and Devices X

DOI:
10.1117/12.2518888

Published: 01/01/2019

Document Version
Publisher's PDF, also known as Version of record

Please cite the original version:

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Ga vacancies and electrical compensation in β-Ga2O3 thin films studied with positron annihilation spectroscopy

Filip Tuomisto, Antti Karjalainen, Vera Prozheeva, Ilja Makkonen, Gunter Wagner, et al.
Ga vacancies and electrical compensation in $\beta$-Ga$_2$O$_3$ thin films studied with positron annihilation spectroscopy

Filip Tuomisto*\textsuperscript{a}, Antti Karjalainen\textsuperscript{a}, Vera Prozheeva\textsuperscript{a}, Ilja Makkonen\textsuperscript{a}, Gunter Wagner\textsuperscript{b}, Michele Baldini\textsuperscript{b}

\textsuperscript{a}Department of Applied Physics, Aalto University, 00076 Aalto, Finland; \textsuperscript{b}Leibniz Institute for Crystal Growth, 12489 Berlin, Germany

ABSTRACT

We have applied positron annihilation spectroscopy to study vacancy-type defects in unintentionally doped and Si and Sn doped $\beta$-Ga$_2$O$_3$ homoepitaxial thin films grown by metal-organic chemical vapor deposition (MOCVD). We detect Ga vacancy related defects at high concentrations in semi-insulating and highly resistive material, while conductive (n-type) material exhibits very low Ga vacancy concentrations. These findings show that Ga vacancies can act as efficient electrical compensators for n-type conductivity, but their concentrations can be suppressed by controlling the growth environment, leading to efficient n-type doping. We also note the strong anisotropy of the positron annihilation signals and give recommendation for presenting positron data obtained in $\beta$-Ga$_2$O$_3$.

Keywords: positron annihilation spectroscopy, gallium oxide, defect, vacancy, compensation

1. INTRODUCTION

When a semiconductor material is doped n-type, the formation of electrically compensating (acceptor-type) native point defects (vacancies, interstitials, and antisites in compound semiconductors) is enhanced. Typically, this is not limiting the carrier concentration for a given dopant concentration, but at very high doping levels issues may arise. The scientifically interesting question is the nature of the dominant native defect that forms and acts as a compensating center for a given type of doping, while the technologically interesting question is whether the formation of this particular defect is limiting the desired functionality. A follow-up question in the case of a positive answer to the latter is whether something can be done to limit the harmful effects of the defect formation. In many materials, vacancy-type defects have the lower formation enthalpies and hence tend to be the dominant compensating defects.

Positron annihilation spectroscopy is an effective method for the investigation of vacancy-type defects in semiconductors.\textsuperscript{1} Positrons implanted in a sample can get trapped in and localize at neutral and negative vacancies due to the missing positive ion core. This results in observable changes in the measurable annihilation characteristics: the positron lifetime, and the momentum distribution of the annihilating positron-electron pair, observed through the Doppler broadening of the positron-electron annihilation radiation. The annihilation data can be used to determine the vacancy concentration as well as to distinguish between different vacancy types and their chemical environment. The method has been successfully applied to elucidate the nature of the dominant compensating acceptors for example in n-type doped semiconductors related to Ga$_2$O$_3$: $V_{Ga}$ in GaN,\textsuperscript{2} $V_{Zn}$ in ZnO,\textsuperscript{3} $V_{In}$ in InN,\textsuperscript{4} and $O_i$ in In$_2$O$_3$.\textsuperscript{5} It is noteworthy that in none of these materials is the compensation of n-type doping an issue. We recently reported\textsuperscript{6} that very high $V_{Ga}$ concentrations in unintentionally doped and Si-doped Ga$_2$O$_3$ thin films coincided with high resistivity or even semi-insulating characteristics, indicating that Ga vacancies could act as efficient compensating defects in Ga$_2$O$_3$.

In this contribution, we extend our previous work\textsuperscript{6} to include unintentionally doped and Sn-doped Ga$_2$O$_3$ MOCVD thin films grown in different conditions and with different source materials. We show that n-type conductive samples contain very low concentrations of Ga vacancy defects, providing further evidence to the $V_{Ga}$ acting as the dominant native acceptor compensating for the n-type doping. Our results also show that by properly choosing the growth conditions and source materials, the $V_{Ga}$ formation and the compensation of n-type conductivity is not an issue in Ga$_2$O$_3$ either, in spite of their very low theoretically calculated formation energies.\textsuperscript{7}
2. EXPERIMENTAL DETAILS

2.1 Ga₂O₃ samples

The thin-film β-Ga₂O₃ samples were prepared using MOCVD in low pressure mode on semi-insulating (100) Ga₂O₃ substrates doped by Mg cut from Czochralski-grown bulk single crystals² AND (010) substrates prepared from EFG grown semi-insulating Ga₂O₃ crystal doped by Fe (Tamura, Japan). All samples were grown at oxygen-rich conditions at 800-850°C, with either trimethylgallium (TMGa) as Ga source and H₂O as oxygen source, or triethylgallium (TEGa) as Ga source and O₂ as oxygen source, to a thickness of 150 – 250 nm. Tetraethylorthosilicate (TEOS) was used as Si source and tetraethyltin (TESn) as Sn source. The homoepitaxial growth resulted in single crystalline material.⁹,¹⁰,¹¹ Basic sample information can be found in Table I. The dopant concentration was measured using secondary ion mass spectrometry employing Si and Sn implanted bulk β-Ga₂O₃ standards. Electrical properties were measured by Hall effect measurements. All the samples grown with TMGa as Ga source were found to be electrically insulating, even the ones with heaviest Si doping, while all the samples grown with TEGa as Ga source were found to be n-type conductive irrespective of doping.

Table I. Basic sample information.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Dopant</th>
<th>Conductivity</th>
<th>Additional information</th>
<th>Orientation</th>
<th>[V_Ga] estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMGa1*</td>
<td>uid</td>
<td>insulating</td>
<td></td>
<td>(100)</td>
<td>1 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>TMGa2*</td>
<td>uid</td>
<td>insulating</td>
<td>annealed in O₂</td>
<td>(100)</td>
<td>5 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>TMGa3*</td>
<td>Si 10¹⁷-10¹⁸ cm⁻³</td>
<td>insulating</td>
<td></td>
<td>(100)</td>
<td>2 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>TEGa1</td>
<td>uid</td>
<td>n-type, low resistivity</td>
<td></td>
<td>(100)</td>
<td>&lt; 1 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>TEGa2</td>
<td>uid</td>
<td>n-type, low resistivity</td>
<td>higher O₂ flux during growth</td>
<td>(100)</td>
<td>2 × 10¹⁶ cm⁻³</td>
</tr>
<tr>
<td>TEGa3</td>
<td>Sn 10¹⁷ cm⁻³</td>
<td>n-type, low resistivity</td>
<td></td>
<td>(100)</td>
<td>1 × 10¹⁶ cm⁻³</td>
</tr>
<tr>
<td>TEGa4</td>
<td>Sn 10¹⁸ cm⁻³</td>
<td>n-type, low resistivity</td>
<td>higher O₂ flux during growth</td>
<td>(100)</td>
<td>3 × 10¹⁶ cm⁻³</td>
</tr>
<tr>
<td>TEGa5</td>
<td>Si 10¹⁸ cm⁻³</td>
<td>n-type, low resistivity</td>
<td></td>
<td>(100)</td>
<td>&lt; 1 × 10¹⁶ cm⁻³</td>
</tr>
<tr>
<td>TEGa6</td>
<td>Si 10¹⁹ cm⁻³</td>
<td>n-type, low resistivity</td>
<td></td>
<td>(010)</td>
<td>&lt; 1 × 10¹⁶ cm⁻³</td>
</tr>
</tbody>
</table>

* The positron annihilation results for these samples have been reported already in Ref. 6.

2.2 Positron annihilation spectroscopy

Positron annihilation spectroscopy is an effective tool for identifying vacancy-type defects in semiconductors.¹ The sensitivity range for neutral and negative vacancies is 10¹⁵–10¹⁹ cm⁻³ (positive vacancies are not detected). In addition to the concentration and open volume, the method can distinguish between different charge states of the vacancies and give information on their chemical environment, i.e. vacancy decorations. In the experiments, positrons are implanted into the specimen where they thermalize and diffuse and eventually annihilate with electrons giving birth to two 511-keV γ-quanta. Prior to annihilation, the positrons probe the sample for vacancies where they can get trapped and localized due to the missing repulsive ion core. Trapping can be observed by measuring the characteristics of the annihilation radiation. The two common measured parameters are the positron lifetime and the Doppler broadening of the annihilation radiation. The former is proportional to the overlap of the wave functions of the positron and electrons of the lattice atoms. The latter displays the momentum distribution of the electrons. Trapping in vacancies increases the average positron lifetime in the sample compared to the defect-free lattice, because the electron density and thus the overlap of the positron and electron wave functions is smaller in a vacancy. The positron lifetime is therefore a measure of the concentration and open volume of the vacancies. In Doppler broadening, the momentum of the annihilating positron-
The electron pair causes a broadening of the 511 keV annihilation line due to energy and momentum conservation. Positrons trapped in vacancies annihilate to a lesser extent with high-momentum core electrons of the atoms than free positrons in the delocalized state in the lattice. Thus, trapping can be seen as the narrowing of the 511 keV line. Doppler broadening gives information on the chemical surroundings of the vacancy, namely the electron configuration of the surrounding atoms, in addition to its concentration.

In this work, we measure the Doppler broadening in the Ga2O3 thin films using a slow positron beam. Positrons from a radioactive source are slowed down and implanted at energies between 0–25 keV. In this energy range the positrons penetrate a layer thickness of up to 1 µm on the average. Because of the relatively poor resolution of the gamma detector, the broadening of the 511-keV annihilation peak is characterized by the so-called $S$ and $W$ parameters, which are defined as the normalized areas (counts) of the center and wings of the peak, respectively. They are a measure of the fraction of positrons annihilating with low-momentum electrons and high-momentum electrons, respectively. The $S$ parameter is a linear superposition of the characteristic $S$ parameters for annihilations in different positron states in the sample:

$$S = \eta_b S_b + \sum_i \eta_i S_i.$$  \hspace{1cm} (1)

Here the subscript $b$ refers to the free, delocalized Bloch state, in which the positron is in the defect-free lattice. The weighting factors $\eta$ are the fractions of positron annihilations at each state. A similar equation holds for the $W$ parameter.

The presence of vacancies therefore results in a higher $S$ parameter and correspondingly a lower $W$ parameter than in the defect-free lattice. If only one type of vacancy (V) traps positrons, $(S,W)$ becomes a linear combination of the values $(S_b,W_b)$ and $(S_V,W_V)$, corresponding to the lattice and the vacancy, respectively. The measured values would thereby fall on a straight line connecting the points $(S_b,W_b)$ and $(S_V,W_V)$ on a $S$-$W$ plot. Also, the vacancy concentration $c_V$ can then be determined, if the positron lifetime $\tau_b$ in the free state (i.e. the positron lifetime in the defect-free lattice) and the so-called trapping coefficient $\mu_V$ of the vacancy are known, using the following formula:

$$c_V = \frac{1}{\mu_V \tau_b} \frac{S - S_b}{S_V - S} = \frac{1}{\mu_V \tau_b} \frac{W - W_b}{W_V - W}.$$  \hspace{1cm} (2)

### 3. RESULTS

Figures 1 and 2 show the $S$ and $W$ parameters measured in a direction perpendicular to the surface normal (within the surface plane) as a function of positron implantation energy (implantation depth) in selected samples, respectively. At low implantation energies, a considerable fraction of the positrons diffuse back to the surface and annihilates there, increasing/decreasing the $S/W$ parameter. Depending on the sample thickness, above implantation energies of 5–10 keV the positrons start penetrating and annihilate in the substrate, which can be seen as a gradual change in the parameters at high energies for the samples where the thin film has a higher/lower $S/W$ parameter than the substrate. The substrate crystals have a low Ga vacancy concentration and the $S/W$ parameters obtained in the substrate are used as reference values for the defect free Ga2O3 lattice (“bulk”).

When the $S$ parameter is higher and correspondingly the $W$ parameter is lower in the thin film than in the bulk, it is a clear indication of the presence of vacancies. To analyze in detail the annihilation parameters and to identify the vacancy defects in question, the $(S,W)$ points representing each thin film are shown in Fig. 3. These layer $(S, W)$-value pairs are determined by taking the corresponding average from the energy range of 2–10 keV, although the exact range was varied from sample to sample to take into account the different layer thicknesses. The error bars indicate the statistical uncertainty within the selected energy range. These values best represent the positron state in each of the thin films. All the points lie on a line connecting the bulk point $(S_b, W_b)$ and the point $(S_V, W_V)$ that has been provisionally identified as representing $V_{Ga}$, for which $S_b/S = 1.066 \pm 0.006$ and $W_b/W = 0.76 \pm 0.02$. Hence we conclude that all the samples contain Ga vacancies. Their concentration varies from sample to sample across the whole sensitivity range, that is from $[V_{Ga}] < 1\times10^{16}$ to $[V_{Ga}] > 5\times10^{19}$ cm$^{-3}$, as listed in Table I. In estimating the concentrations, the values $\mu = 3\times10^{15}$ s$^{-1}$ and $\tau_b = 175$ ps were used in Eq. (2) for the trapping coefficient and the bulk positron lifetime, respectively.\(^6\,^{12}\)
Figure 1. The S parameter measured as a function of the positron implantation energy in selected Ga$_2$O$_3$ thin film samples. The top axis indicates the mean positron implantation depth corresponding to the positron implantation energy.

Figure 2. The W parameter measured as a function of the positron implantation energy in selected Ga$_2$O$_3$ thin film samples. The top axis indicates the mean positron implantation depth corresponding to the positron implantation energy.
4. DISCUSSION

Rather remarkably, the samples can be divided to two groups: those whose $(S, W)$ points are very close to the bulk $(S, W)$ in the upper left corner of Fig. 3, and those whose $(S, W)$ points are close the $V_{Ga}$ $(S, W)$ point (and one sample half-way between the two). This translates into $V_{Ga}$ concentrations of $1–3 \times 10^{16} \text{cm}^{-3}$ (or below) for the first group and to $5 \times 10^{17} \text{cm}^{-3}$ or above for the second group. The one sample in between exhibits a $V_{Ga}$ concentration of about $1 \times 10^{17} \text{cm}^{-3}$. A simple correlation can be observed: whenever the samples are n-type conductive, the $V_{Ga}$ concentrations are low (first group), while semi-insulating or highly resistive samples exhibit Ga vacancy concentrations above $1 \times 10^{17} \text{cm}^{-3}$, and always higher than the concentration of (residual) donors. This observation is the same for the heteroepitaxial (substrate: sapphire) films not shown here, but discussed in detail in Ref. 6. Hence it would appear to be clear that the electrical compensation (or the lack of it) in n-type Ga$_2$O$_3$ is directly related to the presence (or absence) of Ga vacancies.

Both the conductive and semi-insulating groups contain undoped (unintentionally doped) and doped samples. Hence the intentional or residual dopants do not appear to play a decisive role in determining the Ga vacancy formation and the ensuing electrical characteristics. Instead, the source materials are the common denominator in both groups: the conductive samples were grown with TEGa/O$_2$ and the semi-insulating samples with TMGa/H$_2$O. This suggests that the Ga vacancy formation during the thin film growth is controlled by growth kinetics and chemical reactions at the growth surface, instead of thermodynamical processes. The latter are typically more important when bulk crystals are grown in conditions that are closer to the thermodynamic equilibrium. This observation also alleviates the apparent disagreement with theoretical calculations that predict that the formation of $V_{Ga}$ should be strongly favored in n-type material and not in semi-insulating material. One should expect n-type Ga$_2$O$_3$ to contain more $V_{Ga}$ than semi-insulating Ga$_2$O$_3$ only if the growth of the material takes place close to thermodynamic equilibrium.
It should be noted that the VGa-related defects found in the Ga$_2$O$_3$ films are not necessarily isolated. They can be parts of complexes involving oxygen vacancies or donor impurities such as hydrogen or the intentional dopants, or they can be associated with extended defects such as stacking faults. For the intentional dopants and the stacking faults the immediate surroundings of the vacancy are altered very slightly compared to the isolated V$_{Ga}$, and these cannot be directly distinguished from each other with positron annihilation. The differences between V$_{Ga}$, the divacancy V$_{Ga}$-V$_{O}$ and for example V$_{Ga}$ decorated with a single hydrogen atom are likely to be very subtle such as for V$_{Ga}$ in GaN$^{13}$ or V$_Zn$ in ZnO$^{14,15}$ and difficult to distinguish.

A word of caution concerning the quantitative aspects – namely defect concentrations and to some extent the exact identity of the Ga vacancy related defect – of the above discussion is in place. It is important to keep in mind that positron annihilation spectroscopy is a comparative methodology in the sense that detailed defect identification and quantification relies on the availability of reference material where positrons annihilate predominantly in the delocalized state in the “defect-free” lattice, that is, no positron trapping at vacancy defects is observed. So far, systematic studies of positron lifetime in bulk Ga$_2$O$_3$ crystals have not been performed, and hence the reference point (S$_b$, W$_b$) and the bulk lifetime used for both the concentration estimates and defect identification contains more uncertainty than one would hope for. With the lack of more detailed knowledge of positron annihilation in Ga$_2$O$_3$, the above discussion assumes that $\tau_s = 175$ ps in Ga$_2$O$_3$. However, this value and the ensuing conclusion that the Czochralski-grown substrate that exhibits a single positron lifetime of 178 ps at room temperature$^6$ can be assumed to produce annihilation parameters representing the Ga$_2$O$_3$ lattice should be taken with caution, as this interpretation may very well evolve with time when more work is performed. Judging by the present-day knowledge, the possible effects of the re-evaluation of the “bulk” parameters could increase the estimated vacancy concentrations by a factor of 5, and the dominant vacancy-type defects might prove to be larger in open volume than a single V$_{Ga}$.

5. ANISOTROPY IN POSITRON ANNIHILATION SIGNALS

The symmetry, or the lack of thereof, of the crystalline structure causes some anisotropy as a function of measurement direction relative to the crystal orientation in the Doppler broadening experiments. The anisotropy only shows in the (S, W) parameters for the defect-free lattice, as the positron localization at vacancies reduces the overlap of the positron density with the overall crystal structure resulting in isotropic signals. The magnitude of this effect has been extensively studied for example in Si, where the S parameter measured along the (110) direction is 0.2% higher than that measured in the (111) direction.$^{16}$ In ZnO, a difference of up to 1 % has been reported between the S parameters measured along the a and c directions of the wurtzite structure.$^{17}$ Comparing these values with the 6-7% difference between the V$_{Ga}$ and Ga$_2$O$_3$ bulk S parameter values shown in Fig. 3 suggests that this level of anisotropy should not bring significant problems in the interpretation of the experimental observations. However, the diamond and wurtzite lattices have significantly more symmetries than the monoclinic structure of β-Ga$_2$O$_3$ and it is advisable to consider this aspect more closely.

Figure 4 shows the S parameter measured as a function of implantation energy for a (100) sample in two mutually perpendicular directions (A and B) within the (100) plane, and similarly for a (010) sample in two mutually perpendicular directions in the (010) plane. As seen in the figure, the data measured in the (010) plane appears essentially isotropic, but the difference between the directions within the (100) plane is rather dramatic. The S parameter measured along the A and B directions in the (010) plane differs by up to 3 %. This a significant effect, comparable to a difference between vacancy concentrations below the detection limit (less than $10^{16}$ cm$^{-3}$) and roughly $3\times10^{17}$ cm$^{-3}$. Hence this effect must be taken into consideration when performing Doppler broadening experiments in Ga$_2$O$_3$, and the measurement direction needs to be analyzed in detail when presenting S and W parameters. In future reports, it is very important to pay close attention to the measurement direction and give a detailed account of the measurement geometry. Further systematic research into this matter is necessary to fully describe the effects of the low-symmetry Ga$_2$O$_3$ lattice structure on the positron annihilation signals.
SUMMARY

We have performed positron annihilation experiments on β-Ga₂O₃ thin films grown with MOCVD on Czochralski-grown Ga₂O₃ substrates. We detect Ga vacancy related defects at high concentrations in semi-insulating and highly resistive material, while conductive (n-type) material exhibits very low Ga vacancy concentrations. These findings show that Ga vacancies can act as efficient electrical compensators for n-type conductivity, but their concentrations can be suppressed by controlling the growth environment, leading to efficient n-type doping. Importantly, the doping does not directly determine the electrical characteristics, but rather the choice of source materials that governs the growth surface kinetics and hence the Ga vacancy formation. We also note the strong anisotropy of the positron annihilation signals and give a recommendation for presenting positron data obtained in Ga₂O₃.

REFERENCES