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Electrical compensation by Ga vacancies in Ga₂O₃ thin films

E. Korhonen,¹ F. Tuomisto,¹ D. Gogova,² G. Wagner,² M. Baldini,² Z. Galazka,²
 R. Schewski,² and M. Albrecht²

¹Department of Applied Physics, Aalto University, 00076 Aalto, Finland

²Leibniz Institute for Crystal Growth, 12489 Berlin, Germany

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The authors have applied positron annihilation spectroscopy to study the vacancy defects in undoped and Si-doped Ga₂O₃ thin films. The results show that Ga vacancies are formed efficiently during metal-organic vapor phase epitaxy growth of Ga₂O₃ thin films. Their concentrations are high enough to fully account for the electrical compensation of Si doping. This is in clear contrast to another *n*-type transparent semiconducting oxide In₂O₃, where recent results show that *n*-type conductivity is not limited by cation vacancies but by other intrinsic defects such as O_i. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922814>]

Transparent semiconducting oxides (TSOs), such as In₂O₃, SnO₂, ZnO, and Ga₂O₃, combine electrical conductivity with optical transparency which makes them an important material category for electronics and optoelectronics. In highly doped and conducting form (transparent conducting oxides, TCOs), they have applications as transparent contacts in the fields of photovoltaic devices, liquid crystal displays, and light emitting diodes.

Ga₂O₃ has recently generated significant interest and high quality growth (both thin-film and bulk) has been achieved with several techniques.^{1–7} Its distinctive feature compared to other TSOs is the high transparency all the way to UV due to a wide optical 4.9 eV band gap, thus it is a possible material for future UV devices. Ga₂O₃ may crystallize in several different lattice configurations, of which the monoclinic β -Ga₂O₃ is the most commonly considered due to its stability. In a perfect stoichiometric form Ga₂O₃ is an insulator. Extrinsic *n*-doping has been achieved with Sn, while undoped Ga₂O₃ thin films are *n*-type conductive when grown under low O₂ partial pressure.⁸ Oxygen vacancies have been suggested as the origin of intrinsic *n*-type conductivity,⁹ but recent theoretical calculations find V_O to be a deep donor,¹⁰ leaving this question open. Si has been predicted to be an efficient *n*-dopant¹⁰ and Si-doping has been successfully demonstrated with Ga₂O₃ bulk crystals.^{11,12} *p*-doping seems to still elude researchers, similarly to many other TSOs.

In order to use Ga₂O₃ as a semiconductor in electronics, detailed understanding and control of defects and doping are required. Positron annihilation spectroscopy is a powerful method for studying vacancy defects in semiconductors.¹³ In this work, we use positrons to investigate vacancy type defects in undoped and Si-doped Ga₂O₃. We find that the concentrations of Ga vacancy related defects are high enough to fully explain the electrical compensation.

A series of thin-film Ga₂O₃ samples were prepared using Metal-Organic Vapor Phase Epitaxy (MOVPE) in low pressure mode on both *n*-type conductive Ga₂O₃ (series G) substrates cut from Czochralski-grown bulk single crystals,^{3,14} and insulating Al₂O₃ (series A). All samples were grown at oxygen-rich conditions at 800 °C, with trimethylgallium as Ga source, H₂O as oxygen source, and tetraethylorthosilicate as Si source. Growth on Al₂O₃ (0001) resulted in polycrystalline,

yet epitaxial (relationship with the substrate but with in-plane tilt) growth.¹⁵ Homoepitaxial growth resulted in single crystalline material.¹⁶ Growth parameters, most notably Si concentration, were varied for different samples. Basic sample information can be found in Table I. The dopant concentration was measured using secondary ion mass spectrometry employing a Si implanted bulk β -Ga₂O₃ standard. Electrical properties were measured by Hall effect measurements. All thin-film samples were found to be electrically insulating, even the ones with heaviest Si doping.

Positron annihilation spectroscopy is based on implanting the target with positrons and detecting the 511 keV gamma quanta produced by the subsequent electron-positron annihilation. Since positrons are repelled by the positive charge of the atom cores, neutral and negatively charged vacancy defects often act as positron traps. In a vacancy, both the electron density and average electron momentum are reduced compared to the lattice. A positron localized at a vacancy has an increased lifetime as well as an increased probability to annihilate with a low momentum valence electron compared to a delocalized positron. The change in the electron momentum distribution can be seen in the Doppler shift of the annihilation gamma spectrum. To describe the spectrum in a brief fashion, two parameters *S* and *W* are typically used.¹³ *S* is the relative number of counts in the central area of the peak and its value is usually close to 0.5. *W* is the relative number of counts in the high momentum areas on both sides of the peak. Typically, an increase in the value of *S* indicates an increase in open volume defects in the depth being probed, mainly due to the reduced overlap of the positron wavefunction with core electron wavefunctions when the positron is trapped in a vacancy. The value of *W* is more dependent on the type of atoms surrounding the annihilation site.

A variable-energy slow positron beam was used to measure the thin-film samples. The kinetic energy of the positrons was varied to probe varying depths in the samples. The results are shown in Figures 1 and 2 which show the *S* parameter as a function of implantation energy for most of the samples. The corresponding mean implantation depth is marked on the top axis.

Starting from the low energies, the values of the first two data points in the plots are heavily affected by the

TABLE I. Sample thicknesses and dopant concentrations. The MOVPE reactor pressure was 5 mbar for all samples except A5, G1, and G2. Label A stands for Al_2O_3 and G for Ga_2O_3 substrate.

Sample number	d (nm)	[Si] (cm^{-3})	Notes
A1	262	1.0×10^{16}	...
A2	260	2.2×10^{16}	...
A3	251	1.1×10^{17}	...
A4	261	2.5×10^{17}	...
A5	256	3.5×10^{17}	$P_{\text{base}} = 10$ mbar
A6	290	$\approx 10^{17} - 10^{18} \text{ cm}^{-3}$	...
G1	200	...	$P_{\text{base}} = 10$ mbar
G2	200	...	Ann. in 1 atm O_2 at 950°C , $P_{\text{base}} = 10$ mbar
G3	200	...	Ann. in 1 atm O_2 at 950°C
G4	290	$\approx 10^{17} - 10^{18} \text{ cm}^{-3}$	...

surface due to diffusion of thermalized positrons. At 3 keV most of the S -parameters reach their minimum values within the layer area and the surface contribution to the signal is low.

Between 3 and 6 keV the S -value increases slightly to a maximum value in several samples of the A-series. At 6 keV, the mean implantation depth (and the distribution width) is 120 nm. Consequently, a significant fraction of positrons reaches the region at the $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$ heterointerface. This region is likely to contain a higher amount of defects compared to the layer, which is seen as a higher value of S . Other samples lack this effect; G1 and G2 do not even show any plateau in the S -value. The lack of a distinguishable interface state can be attributed to homoepitaxial growth.

The stationary positron diffusion equation was fitted with VEPFIT¹⁷ to the (S , E) and (W , E) data of samples G1 and G2 in order to extract the layer-specific parameters.

FIG. 1. S parameter as a function of implantation energy for a selection of samples grown on Al_2O_3 . The substrate and layer areas are clearly distinguishable. The range marked as “selected area” is used for calculating the layer values for Fig. 3.

A simple model with one layer on top of a substrate was applied. The fitting gave effective positron diffusion lengths of about 10 nm in the Ga_2O_3 thin films and about 100 nm in the substrate. G3 and G4 did not require fitting, as the layer-specific value could be read directly from the data.

Above 6 keV, a higher and higher fraction of positrons is implanted to the substrate. All of the data points eventually converge to either the Al_2O_3 or the Ga_2O_3 substrate value, 0.431 or 0.445, respectively.

For detailed analysis of the positron data, a data point (S , W -value pair) for a low defect density ($< 10^{16} \text{ cm}^{-3}$ vacancies) crystal is very useful as a reference. A positron lifetime measurement¹³ is of particular use for determining this property and it requires a bulk crystal sample. Samples G1 and G4 served as the sample pair for the lifetime measurement with their Ga_2O_3 substrates. The result of the lifetime measurement was a single lifetime of 176 ps with a 260 ps FWHM spectrometer. A similar value has been reported earlier for a free positron in Ga_2O_3 .¹⁸ Hence, it is likely that the Ga_2O_3 substrate produces S and W parameters representative of the Ga_2O_3 lattice and that these can be used as reference values. They are obtained by averaging the S and W data from the energy range (15–23 keV) in the sample G1, giving $S = 0.445$ and $W = 0.0497$. The long positron diffusion length of the substrate obtained above also supports this conclusion.

In order to analyze in detail the differences in annihilation parameters in the Ga_2O_3 layers between different samples, an S - W -plot is shown in Fig. 3. One point was drawn for each sample. These layer (S , W)-value pairs are determined either by taking the corresponding average from the energy range of 2–6 keV, although the exact range was varied from sample to sample to take into account the different layer thicknesses, or from fitting the stationary positron diffusion equation. The error bars indicate the statistical uncertainty within the selected energy range. Thus, these values best represent the positron state in the thin-layer. In Fig. 3, the points lie on a line with the bulk point on the one end and with samples A1 to A4 on the other. The bulk point has the

FIG. 2. S parameter as a function of implantation energy for samples grown on Ga_2O_3 . The solid curves are obtained by fitting the stationary positron diffusion equation to the data.

FIG. 3. S – W -plot with all samples included. One point is drawn per sample for easy comparison. A linear best fit to the points is shown.

lowest S and highest W -values due to positrons annihilating mostly in the free state in the bulk.

A linear change in (S, W) is usually the case when positron trapping is dominated by one defect type. The vacancy in question must be Ga-related since single oxygen vacancies are too small to trap positrons in addition to usually being positively charged.¹⁹ The simplest explanation is that single gallium vacancies (V_{Ga}) are detected, although complexes of V_{Ga} with V_{O} are possible as well.

Several of the samples in the heteroepitaxial A series (A1–A4) form a tight cluster near the low right corner with $S=0.471$ – 0.475 and $W=0.038$. Changing the Si-doping concentration has very little effect on the positron results as long as other growth parameters are kept constant. It is likely that the cluster of points represents the vacancy state with all positrons being trapped to vacancies in the corresponding samples. Comparing the S and W -values of this state ($S_{\text{D}}, W_{\text{D}} = [0.474(2), 0.038(1)]$) with those of the bulk state ($S_{\text{B}}, W_{\text{B}} = [0.445(1), 0.050(1)]$) gives the characteristic value $S_{\text{D}}/S_{\text{B}} = 1.066(6)$ and $W_{\text{D}}/W_{\text{B}} = 0.76(2)$. Similar values (1.058 and 0.76) have been measured for V_{Ga} in GaN,²⁰ a material with constituent atom sizes close to those of Ga_2O_3 . In addition, the vacancy signal gets stronger with annealing in O_2 , supporting this interpretation. Saturation trapping implies that the V_{Ga} concentration in the samples A1–A4 is at least $5 \times 10^{18} \text{ cm}^{-3}$.¹³

Samples of the homoepitaxial G-series, as well as A5 and A6, fall between the line endpoints. The layer of sample G1 is clearly closest to the bulk point. This sample was not treated in any way after growth. The annealed samples G2 and G3 are significantly further away and give practically identical results. A5 and A6 have similar growth parameters but were grown in different batches. Finally, G4 is a homoepitaxial version of A6 and is located a bit further down the line. The vacancy concentration of these samples can be estimated by comparing the annihilation parameters to those of the defect and the defect-free lattice as in Ref. 21. In G1, the concentration is $1 \times 10^{17} \text{ cm}^{-3}$, in G2 and G3 $5 \times 10^{17} \text{ cm}^{-3}$, and finally in A5, A6, and G4 in the 1 – $2 \times 10^{18} \text{ cm}^{-3}$ range. Both annealing in O_2 and Si doping strongly increase the concentration of Ga vacancies in the samples.

All thin-film samples were found to be electrically insulating despite significant Si-doping. The Ga vacancy concentration is highest in the samples A1–A4 that were Si-doped from 10^{16} to 10^{17} cm^{-3} . This is less than the estimated Ga vacancy concentration ($> 5 \times 10^{18} \text{ cm}^{-3}$). Theoretical calculations predict that the V_{Ga} should be in a negative charge state for Fermi levels in the upper half of the band gap,²² compensating for n -type doping. Hence, the observed Ga vacancy concentrations in the Ga_2O_3 films fully account for the compensation of Si doping. In addition, the n -type conductive substrate does not contain a significant concentration of Ga vacancies, in line with this conclusion.

In summary, homo- and heteroepitaxial undoped and Si-doped Ga_2O_3 thin films were studied using positron annihilation spectroscopy. All samples show a significant (above 10^{17} cm^{-3}) concentration of Ga vacancies, enough to fully explain the electrical compensation. Interestingly, this finding is opposite to that in In_2O_3 ,²¹ where n -type conductivity is not limited by cation vacancies but by other intrinsic defects such as O_i .

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