Gallium vacancy and the residual acceptor in undoped GaSb studied by positron lifetime spectroscopy and photoluminescence

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Positron lifetime, Photoluminescence and Hall measurements were performed to study undoped p-type gallium antimonide materials. A 314ps lifetime component, attributed to \( V_{Ga} \) related defect, was identified in the positron lifetime measurement. In the PL measurement, a 778meV and a 797meV peaks were observed. Isochronal annealing studies were performed and at the temperature of 300°C, both the 314ps positron lifetime component and the two PL signals disappeared, which gives a clear and strong evidence for their correlation. However, the hole concentration \( (\sim 2 \times 10^{17} \text{cm}^{-3}) \) was observed to be constant throughout the whole annealing temperature range up to 500°C. Contradictory to general belief, this implies, at least for samples with annealing temperatures above 300°C, the Ga vacancy is not the acceptor responsible for the p-type conduction.

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Gallium Antimonide is the basic material for a variety of lattice parameter matched III-V compounds having band gaps ranging from 0.3eV to 1.58eV (corresponding to wavelengths of 0.8 to 4.3µm) (See reviews \[1, 2\]). Thus, GaSb and its lattice matched materials are capable of fabricating optoelectronic devices operating in a wide range of wavelength, high frequency devices and thermophotovoltaic devices. Undoped GaSb materials are p-type conducting having a hole concentration of \( 10^{16} - 10^{17} \text{cm}^{-3} \). For the PL studies of such material \[3, 4, 5, 6, 7\], a luminescence signal called band A (peak at 778meV) is commonly found irrespective of growth method. This signal and also the residual acceptor were attributed to the \( V_{Ga} \) related defect, though no further direct evidence for this assignment had been observed. In this study, we have studied undoped p-type GaSb materials using positron lifetime spectroscopy, photoluminescence and Hall measurement, particular with an intention to study the correlation between the PL signals, the Ga vacancy and the hole concentration.

Samples were cut from two different LEC grown undoped GaSb wafers (namely called GaSb042Un with \( p = 2.5 \times 10^{16} \text{cm}^{-3} \) and GaSb342Un with \( p = 2.0 \times 10^{17} \text{cm}^{-3} \)) commercially purchased from the MCP Wafer Technology Ltd. Each of the isochronal annealing process was carried out in forming gas (\( N_{2} : H_{2} = 80\% : 20\% \)) for a period of 30 minutes. After the annealing, the samples were moved to a room temperature region while still kept in the forming gas atmosphere before they were cooled down and removed from the furnace. Details of positron lifetime measurement were as reported in \[8\]. The 4-million-count positron lifetime spectra collected with a fast-fast positron lifetime spectrometer having a resolution of fwhm=230ps were analyzed by the source code POSITRONFIT \[10\], in which the measured spectra were fitted by the equation: \( \sum_{i} I_{i} \exp(-\lambda_{i} t) \), where \( I_{i} \) and \( \tau_{i} = 1/\lambda_{i} \) are the intensity and the characteristic positron lifetime of the corresponding annihilation site, with the consideration of the instrumental convolution and background contribution. The PL measurements were performed at 10K and the details can be found in Mui et al \[9\].

Before discussing the positron lifetime results of the undoped GaSb samples, it is interest to note our previous results of a positron lifetime study on a heavily Zn-doped GaSb sample (GaSb098Zn) having \( p = 3.28 \times 10^{18} \text{cm}^{-3} \) reported in Ref. \[8\]. Referring to Ref. \[8\], a two-component model was found to well describe the spectra in the as-grown sample. The long lifetime component having characteristic lifetime of \( \tau_{2} = 318 \pm 7 \text{ps} \) was attributed to positrons annihilating at \( V_{Ga} \) related defects. Isochronal annealing studies of the Zn-doped sample indicated there were two annealing stages, namely starting at 300°C and 580°C, and the average positron lifetime is also plotted in figure 1 for reference. According to Ref. \[8\], the drop in average lifetime at 300°C in figure 1 was shown to correspond with an increase of the long lifetime component.
which was attributed to Ga vacancy related defect [8]. Also close to the 318 ps found in the Zn-doped sample, 266 ps, which is coincident with that in Ref. [8]. The 314 ps trapping process was observed and the bulk lifetime is 370 ps having a lifetime of 314 ps was annealed out at about 400 °C. This implies the positron trapping centre has a lifetime of 314 ps. At annealing temperature drops to about 266 ps. The spectra of the undoped samples were also fitted with the source code POSITRONFIT. It was found that at an annealing temperature lower than 370 °C, a two component model was found to offer a good fit to the spectra and the long lifetime component was constant at 314 ps. At annealing stage at temperature of 300 °C – 400 °C, for which the average lifetime drops to about 266 ps. The spectra of the undoped samples were also fitted with the source code POSITRONFIT. It was found that at an annealing temperature lower than 370 °C, a two component model was found to offer a good fit to the spectra and the long lifetime component was constant at 314 ps. At annealing temperatures higher than 370 °C, a single component model with lifetime of 266 ps was employed to give good fit to the data. This implies the positron trapping centre having a lifetime of 314 ps was annealed out at about 370 °C. Above this annealing temperature, no positron trapping process was observed and the bulk lifetime is 266 ps, which is coincident with that in Ref. [8]. The 314 ps lifetime component identified in the undoped samples is also close to the 318 ps found in the Zn-doped sample, which was attributed to Ga vacancy related defect [8].

from 318 ps to 379 ps and a decrease of the long lifetime intensity from 50% to 15%. This was argued to be related to the annealing out of the V_{Ga} related defect and the formation of a new defect having a lifetime of 379 ps. At the 580 °C annealing stage, the lifetime spectrum became containing only one component with value of 267 ps. In Ref. [8], it was also shown that the GaSb bulk lifetime obtained from considering the temperature varying experiment of the as-grown sample and the isochronal annealing studies agreed with each other at a value of 267 ps.

The positron average lifetime as a function of the annealing temperature measured at room temperature for the two undoped GaSb samples are shown in figure 1 and they have very similar behaviors. There is an annealing stage at temperature of 300 °C – 400 °C, for which the average lifetime drops to about 266 ps. The spectra of the undoped samples were also fitted with the source code POSITRONFIT. It was found that at an annealing temperature of 370 °C, a two component model was found to offer a good fit to the spectra and the long lifetime component was constant at 314 ps. At annealing temperatures higher than 370 °C, a single component model with lifetime of 266 ps was employed to give good fit to the data. This implies the positron trapping centre having a lifetime of 314 ps was annealed out at about 370 °C. Above this annealing temperature, no positron trapping process was observed and the bulk lifetime is 266 ps, which is coincident with that in Ref. [8]. The 314 ps lifetime component identified in the undoped samples is also close to the 318 ps found in the Zn-doped sample, which was attributed to Ga vacancy related defect [8].

Furthermore, the annealing behaviors of the 314 ps component in the undoped samples and the 318 ps component in the Zn-doped sample are very similar (annealing behavior of V_{Ga} related defect in Zn-doped sample published in Ref. [8] is also included as symbol triangle in figure 2(a) for reference). It is thus plausible to conclude the 314 ps component found in the undoped GaSb samples at annealing temperatures lower than 370 °C is due to V_{Ga} related defect and it disappears at an annealing temperature of 370 °C.

With the simple trapping model [e.g. Ref. [1]], the positron trapping rate of the V_{Ga} defect $\kappa$ is related to the characteristic defect lifetime $\tau_d$, the bulk lifetime $\tau_{bulk}$ and the average lifetime $\tau_{ave}$ as: $\kappa = (\tau_{ave} / \tau_d - \tau_{ave}) = \mu / c$, where $\mu$ and $\kappa$ are the concentration and the specific positron trapping coefficient of $V_{Ga}$. Although the precise value of $\mu$ for the Ga vacancy in GaSb is still not available, based on the specific positron coefficient values of $V_{Ga}^-$ in GaAlSb and $V_{Ga}^-$ in GaAs, the specific positron trapping coefficient for $V_{Ga}$ in GaSb was estimated to be $\mu \sim 2 \times 10^{14} \text{s}^{-1}$ [8]. The calculated Ga vacancy concentrations of the two undoped GaSb samples as a function of the annealing temperature are shown.
in figure 2(a). It is clearly seen that the Ga vacancy in all the three samples has a concentration of $\sim 10^{17}\text{cm}^{-3}$ and disappears at the temperature range of 300°–400°C.

The PL spectra of the two undoped sample are very similar and those of GaSb042Un annealed at different temperatures are shown in figure 3. From the figure, two dominant luminescence peaks were observed to be at about 780meV and 800meV. At the low energy shoulder of the 780meV peak, there is another weak luminescence signal at about 760meV. It is also obvious that the PL signals were greatly reduced by the 300°C annealing. The PL spectra were fitted with the superposition of three Gaussians and all the fitted curves have excellent values of chi-square. The fitted peak positions of the two dominant signals are found to be constants at different annealing temperatures with values of 777.4 ± 0.7meV and 798.8 ± 1.7meV for GaSb042Un, and 778.3 ± 1.5eV and 794.7 ± 2.6eV for GaSb342Un. The intensities of the two peaks for both undoped samples as a function of the annealing temperature are shown in figure 2(b) and (c). One notes that the annealing behavior of the Ga vacancy related defect detected by the positron lifetime technique is effectively the same as that of the two PL signals. This is a clear and strong evidence suggesting that the 314ps positron lifetime component, the 778meV and the 797meV PL signals are originated from the same $V_{Ga}$ related defect.

The 778meV PL signal is commonly observed in most of the p-type GaSb materials and is known as the band A. The residual acceptor responsible for p-type conduction of undoped material and the band A PL signal were observed to be related to the Ga excess and the band A PL signal is usually associated to CB or donor to $V_{Ga}$ transition. The other dominant PL peak lines 795 to 799meV seen in the present study has been previously reported and attributed to exciton bound to neutral $V_{Ga}Ga_{Sb}$. The present observed evidence for the correlation between the two dominant PL peaks (778meV and 797meV) and the Ga vacancy as seen from the positron lifetime signal strongly supports the general believed physical processes for luminescence.

In order to study the correlation between the Ga vacancy and the hole concentration, the hole concentrations of the GaSb342Un sample annealed at different temperatures were measured by Hall measurement at room temperature (results shown in figure 2(d)). The hole concentration is about $2 \times 10^{17}\text{cm}^{-3}$ at all different annealing temperatures, which is consistent with the observation of stable hole concentration upon annealing reported by Effer and Etter. In the work of Van Der Meulen, it was pointed out the residual acceptor was related to the Ga excess and contained a vacancy in its structure. It was further argued that because of its lack of mobility and stability upon annealing, the residual acceptor must be a $V_{Ga}Ga_{Sb}$. However, from the annealing behavior of the lifetime signal and the hole concentration shown in figure 2(a) and (d), at least for undoped samples annealed at 300°C ($V_{Ga}$ anneals out) or above, the p-type conduction is not originated from the Ga vacancy, but is from another acceptor. This observation somehow contradicts the general belief that $V_{Ga}Ga_{Sb}$ is always the acceptor contributing the holes to the valance band for undoped GaSb.

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