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

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Positron lifetime, photoluminescence (PL), and Hall measurements were performed to study undoped *p*-type gallium antimonide materials. A 314 ps positron lifetime component was attributed to Ga vacancy (V_{Ga}) related defect. Isochronal annealing studies showed at 300 °C annealing, the 314 ps positron lifetime component and the two observed PL signals (777 and 797 meV) disappeared, which gave clear and strong evidence for their correlation. However, the hole concentration ($\sim 2 \times 10^{17} \text{ cm}^{-3}$) was observed to be independent of the annealing temperature. Although the residual acceptor is generally related to the V_{Ga} defect, at least for cases with annealing temperatures above 300 °C, V_{Ga} is not the acceptor responsible for the *p*-type conduction. © 2002 American Institute of Physics. [DOI: 10.1063/1.1482419]

Gallium antimonide is the basic material for a variety of lattice parameter matched III–V compounds having band gaps ranging from 0.3 to 1.58 eV (corresponding to wavelengths of 0.8 to 4.3 μm) (See Refs. 1 and 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} cm^{-3} . For the PL studies of such material,^{3–6} a luminescence signal called band A (peaking at 778 meV) is commonly found irrespective of growth method. This signal and also the residual acceptor were related to Ga in excess and were generally considered as being due to the $V_{\text{Ga}}\text{GaSb}$ defect,^{1–7} 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 (PL), and Hall measurement, in particular with an intention to study the correlations among the PL signals, the Ga vacancy, and the hole concentration.

Samples were cut from two different liquid encapsulated Czochralski (LEC) grown undoped GaSb wafers (namely, GaSb042Un with $p = 2.5 \times 10^{17} \text{ cm}^{-3}$ and GaSb342Un with $p = 2.0 \times 10^{17} \text{ cm}^{-3}$) commercially purchased from the MCP Wafer Technology Ltd. Each isochronal annealing process was carried out in forming gas ($\text{N}_2:\text{H}_2 = 80\%:20\%$) for a period of 30 min. 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 mea-

surement were as reported in Ref. 8. The 4-million-count positron lifetime spectra collected with a fast-fast positron lifetime spectrometer having a resolution of $\text{fwhm} = 230 \text{ ps}$ were analyzed by the source code POSITRONFIT,⁹ 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, respectively, with the consideration of the instrumental convolution and background contribution. The PL measurements were performed at 10 K, and the details can be found in Mui *et al.*¹⁰

Before discussing the positron lifetime results of the undoped GaSb samples, it is of 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 and 580 °C, the average positron lifetime is plotted in Fig. 1 for reference. According to Ref. 8, the drop in average lifetime at 300 °C in Fig. 1 was shown to correspond with an increase of the long lifetime component from 318 to 379 ps and with 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 changed to one containing only a single component with value of 267 ps. In Ref. 8, it was also shown that, with respect to the GaSb bulk lifetime obtained from considering the as-grown sample

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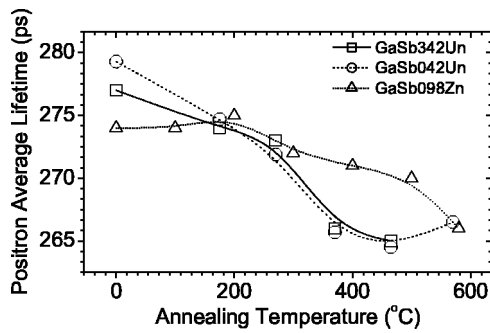


FIG. 1. Average positron lifetime of the undoped GaSb samples GaSb042Un (○) and GaSb342Un (□) as a function of the annealing temperature. The average lifetime data of the Zn-doped sample GaSb098Zn (△) presented in Ling *et al.* is also included here for comparison.

temperature-varying experiment, 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 is shown in Fig. 1, and they have very similar behaviors. There is an annealing stage at temperature of 300–400 °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 before this annealing stage, a two-component model was found to offer a good fit to the spectra and the long lifetime component was constant at 314 ps. Above this annealing stage, a single-component model with lifetime of 266 ps was employed to give good fit to the data. This implies the positron trapping center having a lifetime of 314 ps was annealed out and no positron trapping process was observed. The bulk lifetime is thus equal to the value of the single lifetime component, i.e., 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 a 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 a V_{Ga} related defect and it disappears at annealing temperature of 300–400 °C.

With the simple trapping model (e.g., Ref. 11), the positron trapping rate of the V_{Ga} defect κ is related to the characteristic defect lifetime τ_d , the bulk lifetime τ_{bulk} , and the average lifetime τ_{ave} as: $\kappa = [\tau_{ave} - \tau_b] / [\tau_b(\tau_d - \tau_{ave})] = \mu \times c$, where c and μ are the concentration and the specific positron trapping coefficient of V_{Ga} , respectively. Although the precise value of μ 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 Fig. 2(a). It is clearly seen that the Ga vacancy in all the three samples has a concentration

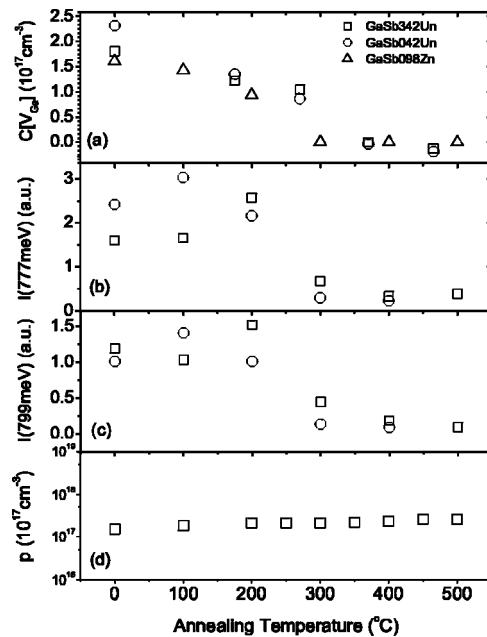


FIG. 2. (a) Concentration of the V_{Ga} defects in the undoped GaSb samples calculated from the positron lifetime data as a function of the annealing temperature. (b) and (c) Peak intensities and positions of the two significant PL signals observed in the undoped GaSb samples as a function of the annealing temperature. (d) Hole concentration as a function of the annealing temperature.

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 Fig. 3. From the figure, two dominant luminescence peaks were observed to be at about 780 and 800 meV. At the low energy shoulder of the 780 meV peak, there is another weak luminescence signal at about 760 meV. 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 were found to be constants at different annealing temperatures with values of 777.4 ± 0.7 and 798.8 ± 1.7 meV for GaSb042Un, and 778.3 ± 1.5 and 794.7 ± 2.6 eV for GaSb342Un. The intensities of the two peaks for both undoped samples as a function of the annealing temperature are shown in Figs. 2(b) and 2(c). One notes that the annealing behavior of the Ga vacancy related defect

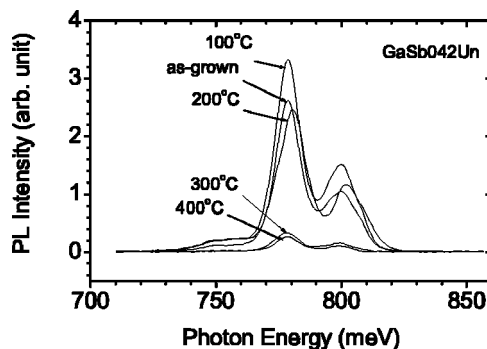


FIG. 3. PL spectra of the undoped sample GaSb042Un annealed at different temperatures.

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 314 ps positron lifetime component, the 778 and the 797 meV PL signals are originated from the same V_{Ga} related defect.

The 778 meV 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.^{3-5,7} The residual acceptor is usually attributed to the $V_{\text{Ga}}\text{Ga}_{\text{Sb}}$ defect⁷ and the band A PL signal is usually associated with conduction band (CB) or donor to $V_{\text{Ga}}\text{Ga}_{\text{Sb}}$ transition.³⁻⁶ The other dominant PL peak lines 795 to 799 meV seen in the present study have been previously reported and are attributed to exciton bound to neutral $V_{\text{Ga}}\text{Ga}_{\text{Sb}}$.⁴⁻⁶ The present observed evidence for the correlation between the two dominant PL peaks (778 and 797 meV) and the Ga vacancy as seen from the positron lifetime signal strongly supports the generally 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 Fig. 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.¹² In the work of Van Der Meulen,⁷ 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 $V_{\text{Ga}}\text{Ga}_{\text{Sb}}$. The annealing behavior of the hole concentration shown in Fig. 2(d) is consistent with the reported thermal stable hole concentration. However, from the annealing behaviors of the lifetime signal and the hole concentration shown in Figs. 2(a) and 2(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.

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