

## Undoped gallium antimonide studied by positron annihilation spectroscopy

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### ABSTRACT

Positron lifetime spectroscopy has been used to study the vacancy type defects in undoped gallium antimonide. Temperature dependent positron trapping into the  $V_{Ga}$ -related defect having a characteristic lifetime of 310ps was observed in the as-grown sample. The lifetime data were well described by a model involving the thermal ionization (0/-) of the  $V_{Ga}$ -related defect and its ionization energy was found to be  $E(0/-) = 83\text{meV}$ . For the electron irradiated sample, the  $V_{Ga}$ -related defect with lifetime of 310ps that was found in the non-irradiated samples was also identified. Moreover, another lifetime component (280ps) was only observed in the electron irradiated sample but not in the non-irradiated sample. It was also attributed to the  $V_{Ga}$ -related defect. The two identified  $V_{Ga}$ -related defects should have different microstructures because of their difference in characteristic lifetimes. The 280ps component remains thermally stable after the 500°C annealing while the 310ps component anneals at 300°C.

### I. INTRODUCTION

Gallium antimonide (GaSb) is a III-V semiconductor having a narrow direct band gap ( $\sim 0.75\text{eV}$  at 300K) that can be used in fabricating high frequency and long wavelength optoelectronic devices. Undoped GaSb is usually p-type having a hole concentration of  $\sim 10^{16}$ - $10^{17}\text{cm}^{-3}$ . The residual acceptor responsible for the p-type conduction was reported to be doubly ionized, to be related to Ga in excess and has been attributed to  $Ga_{Sb}$ ,  $V_{Ga}$  or  $V_{Ga}Ga_{Sb}$  related defects [1-5]. Detailed reviews of this material can be found in references [1] and [2].

Positron annihilation spectroscopy (PAS) is a nondestructive probe selectively sensitive to neutral or negatively charged open volume defects in semiconductors [6]. Open volume defects, like vacancy, are positron trapping centers as they present as a potential well to the positron in the solid. The positron in the solid will thus finally annihilate with an electron either in the delocalized bulk state or in the localized defect state. The principle of PAS is that the outgoing annihilation gamma photons carry the information of the electronic environment at which the positron annihilates.

Although extensive PAS studies have been performed on III-V semiconductors, little work has been carried out on the GaSb material [7-11]. In our previous studies [10,11], a 315ps positron lifetime component was identified in heavily Zn-doped and undoped GaSb materials

and it was attributed to the  $V_{Ga}$ -related defect. This defect annealed at the temperature of  $\sim 300^{\circ}C$ . Furthermore, we have also observed the correlation between the annealing of the 777meV PL signal (band A) and that of the 315ps lifetime component (the  $V_{Ga}$ -related defect). Furthermore, the disappearance of the 315ps lifetime signal at  $300^{\circ}C$  and the thermal stability of the hole concentration up to  $500^{\circ}C$  suggests that the 315ps lifetime component is not the residual acceptor [11].

In this paper, electron irradiated ( $1.7MeV$  and dosage  $10^{16}cm^{-3}$ ) and as-grown undoped GaSb samples were studied by positron lifetime technique. Temperature dependent lifetime measurements were performed on the as-grown sample in order to study the thermal ionization of the 315ps positron trap (i.e. the  $V_{Ga}$ -related defect). For the electron irradiated sample, we have performed an isochronal annealing study up to the temperature of  $500^{\circ}C$ .

## II. EXPERIMENTAL SETUP

Samples pieces with size of  $1 \times 1 cm^2$  were cut from the liquid encapsulated Czochralski (LEC) grown undoped GaSb wafer purchased from the MCP Wafer Technology Ltd., U.K. This wafer is identical to the one that has been used in our previous studies. Two pieces of the samples were then irradiated with  $10^{16}cm^{-2}$   $1.7MeV$  electrons and another pair of samples remained non-irradiated. Each of the annealing step of the electron irradiated sample was performed in the forming gas atmosphere ( $N_2:H_2=80\%:20\%$ ) for a period of 30 minutes. The positron source was directly deposited  $^{22}NaCl$  onto one piece of the sample and then was sandwiched by the other piece. The positron lifetime spectrometer has a resolution of  $fwhm=230ps$ . To carry out the temperature dependent lifetime measurement, the sample-source assembly was installed into a 10K Oxford closed cycle He cooling system. Each of the lifetime spectra contained  $4 \times 10^6$  counts. The normalized positron lifetime spectrum  $S(t)$  can be represented by the linear combination of the exponential terms contributed from the annihilating sites [12]:  $S(t) = \sum_i I_i \exp(-t/\tau_i)$ , where  $I_i$  and  $\tau_i$  are the intensity and the characteristic lifetime of the  $i$ -th annihilation site. The spectra were decomposed by the source code POSITRONFIT [12] according to this equation.

## III. RESULTS AND ANALYSIS

### A. Temperature dependent lifetime studies of as-grown undoped GaSb

The measured positron average lifetime  $\tau_{ave}$  (defined as:  $\sum I_i \tau_i = \int tS(t)dt / \int S(t)dt$ ) of the as-grown undoped sample as a function of the measuring temperature is shown in figure 1. From figure 1, the average lifetime increases with increasing temperature. The two-component model was found to give good representation to all of the spectra. The long lifetime component, which is the vacancy component, was found to have a constant characteristic lifetime of 310ps irrespective of the measuring temperature. This 310ps lifetime is close to the value of the  $V_{Ga}$ -related defect found in our previous studies [10,11] and was thus attributed to the same defect.

The increase of the observed average lifetime with respect to temperature can be explained by the change of the charge state occupancy of the  $V_{Ga}$ -related defect. As temperature

increases, the Fermi level moves away from the valence band and thus the  $V_{Ga}$ -related defects possess a more negative occupancy. This implies these  $V_{Ga}$ -related defects become more efficient positron trapping centers. Thus, more positrons annihilate in the defect state, which has a longer lifetime than that of the bulk state, and the average lifetime increases. The charge state occupancy of the  $V_{Ga}$ -related defect is given by [6]:

$$\frac{[V_{Ga}^Q]}{[V_{Ga}^{Q+1}]} = \frac{g_Q}{g_{Q-1}} \exp\left[-\frac{(E_i - E_F)}{kT}\right] \quad (1)$$

where  $[V_{Ga}^Q]$  is the concentration of the  $V_{Ga}$ -related defect possessing the charge of  $Q$  and  $E_i$  is the ionization energy of the ionization process  $V_{Ga}^Q + e^- \leftrightarrow V_{Ga}^{Q-1}$ .  $g_Q$  is the degeneracy of the state  $V_{Ga}^Q$ . The charge occupancies of different charge states (i.e.  $[V_{Ga}^Q]/[V_{Ga}]$ ), where  $[V_{Ga}]$  is the total concentration of  $V_{Ga}$  at given temperature and  $E_F$  position can then be calculated by using equation (1) and:

$$[V_{Ga}] = \sum_Q [V_{Ga}^Q] \quad (2).$$

The Fermi level at different temperatures were calculated from the hole concentration data obtained from the temperature dependence hall (TDH) measurement using the relation:  $p = N_V \exp[-(E_F - E_V)]$ , where  $N_V$  is the effective density of states of valance band.

In order to model positron trapping into the  $V_{Ga}$ -related defects having different charge states, the simple trapping model [6] was employed. In the simple trapping model, positrons initially in the delocalized state may transit to the  $V_{Ga}^Q$  state with trapping rate of  $\kappa_Q$  or may annihilate in the delocalized state with the annihilation rate of  $\lambda_b = 1/\tau_b$ , where  $\tau_b$  is the positron lifetime of the bulk. The trapping rate  $\kappa_Q$  is given by:  $\kappa_Q = \mu_Q [V_{Ga}^Q]$ , where  $\mu_Q$  is the specific positron trapping coefficient of the defect  $V_{Ga}^Q$ . For neutral vacancy, the specific trapping coefficient is independent of temperature and that of the negatively charged vacancy follows the temperature dependence of  $\sim T^{-0.5}$  [6,13]. For the positron in the  $V_{Ga}^Q$  state, positron detrapping (i.e. transiting back to the bulk state) is assumed to be forbidden because of its relatively large binding energy ( $\sim 1\text{eV} \gg kT$ ) and thus it will annihilate with the rate of  $\lambda_Q = 1/\tau_Q$ , where  $\tau_Q$  is the characteristic positron lifetime of the defect  $V_{Ga}^Q$ . The rate equations to describe the positron state transition and annihilation can thus be written as [6]:

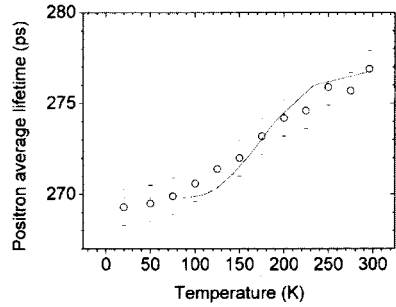


Figure 1 Average positron lifetime of the as-grown undoped GaSb sample as a function of the measurement temperature.

$$\frac{dn_b}{dt} = -\sum_i \kappa_i n_b - \lambda_b n_b \quad (3)$$

$$\frac{dn_Q}{dt} = \kappa_Q n_b - \lambda_Q n_Q, \quad Q = \dots - 2, -1, 0, +1, +2, \dots$$

Solving these rate equations yields a positron lifetime spectrum having the form  $S(t) = \sum_i I_i \exp(-t/\tau_i)$ , whereas the lifetime parameters  $\tau_i$  and  $I_i$  are functions of  $\kappa_i$ 's and  $\lambda_i$ 's. For example, if there are two charge states (say, 0 and -), it can be shown that the resultant lifetime spectrum consists of three components with the lifetime parameters given as [6]:

$$I_1 = 1 - I_2 - I_3 \quad (4)$$

$$I_2 = \frac{\kappa_-}{\kappa_- + \kappa_0 + \lambda_b - \lambda_-} \quad (5)$$

$$I_3 = \frac{\kappa_0}{\kappa_- + \kappa_0 + \lambda_b - \lambda_0} \quad (6)$$

$$\tau_1 = \frac{1}{\lambda_b + \kappa_- + \kappa_0} \quad (7)$$

$$\tau_2 = \frac{1}{\lambda_d} \quad (8)$$

$$\tau_3 = \frac{1}{\lambda_{d0}} \quad (9)$$

where  $\kappa_-$  and  $\kappa_0$  are the trapping rates of  $V_{Ga}$  and  $V_{Ga}^0$ , respectively.  $\lambda_b = 1/\tau_b$ ,  $\lambda_- = 1/\tau_-$  and  $\lambda_0 = 1/\tau_0$  are the positron annihilation rates of the bulk, the negative charged and the neutral states, respectively.

The above model was used to fit for the positron average lifetime data shown in figure 1. The GaSb bulk lifetime was taken as 267ps. As it has already been pointed out the lifetime of defect component was found to be constant at 310ps, the characteristic lifetime of the  $V_{Ga}$  related defect was taken to be 310ps irrespective of the charge state. Although there are no previously reports on the specific trapping coefficient of  $V_{Ga}$  in GaSb, value of  $\mu \sim 1 \times 10^{15} s^{-1}$  was reported for  $V_{Ga}^-$  in AlGaSb at 300K [14]. The ratio of the specific trapping coefficients between the neutral and the negative state of the same vacancy was found to be 1:5 [13]. Thus, the specific trapping coefficients at 300K for  $V_{Ga}^0$  and  $V_{Ga}^-$  were  $\mu_0 \sim 2 \times 10^{14} s^{-1}$  and  $\mu_- \sim 1 \times 10^{15} s^{-1}$ , respectively. We have attempted different possibilities of  $V_{Ga}$  ionizations carrying charges from +1 to -3 and observed that the data in figure 1 can be well fitted by the model involving a single ionization:  $V_{Ga}^0 + e^- \leftrightarrow V_{Ga}^-$  with the ionization energy given by  $E(0/-) = 83meV$  and the  $V_{Ga}^-$  related defect concentration given by about  $5 \times 10^{16} cm^{-3}$ . The modeled curve is plotted in figure 1 with the solid line. This implies the Ga vacancy is not the residual acceptor of the present undoped GaSb samples, which have hole concentration of the order of  $\sim 10^{17} cm^{-3}$ . This conclusion is consistent with those in references [11,15,16].

## B. Isochronal annealing lifetime study of electron irradiated undoped GaSb

Isochronal annealing lifetime studies were also performed on the electron irradiated ( $1.7\text{MeV}$  and dosage  $10^{16}\text{cm}^{-2}$ ) undoped GaSb (gasb042un) sample. For each annealing step, positron lifetime measurements were carried out on the sample at room temperature. The average positron lifetime of the sample as the function of the annealing temperature is shown in figure 2(a). The average lifetime decreases with annealing temperature, reaches the minimum at  $200^\circ\text{C}$  and then increases with increasing annealing temperature.

We have also attempted to fit the spectra with the two-component model, which gives good representation only to the spectra of the sample annealed at  $300^\circ\text{C}$  or above and the long lifetime component has constant lifetime of about  $280\text{ps}$ . For the spectra of the sample annealed below  $300^\circ\text{C}$ , the two component model fails to give good fit to the spectra and the three component model is required. For such spectra, the two long lifetime (i.e. defect) components were found to be constant at about  $315\text{ps}$  and  $280\text{ps}$  independent of the annealing temperature.

The fitted intensities of the two defect components are shown in figure 2(b). From the figure, the  $315\text{ps}$  component intensity decreases with annealing temperature and vanishes after  $300^\circ\text{C}$  annealing. The characteristic lifetime and the annealing behavior of this component is very similar to those of the  $V_{\text{Ga}}$ -related defect identified in the non-irradiated undoped GaSb samples (previous section and refs. [10,11]). For the  $280\text{ps}$  component which cannot be found in the non-irradiated undoped GaSb samples, its intensity increases with annealing temperature and saturates at about  $300^\circ\text{C}$ . It remains thermally stable up to  $500^\circ\text{C}$  annealing. The defect lifetime to the bulk lifetime ratio  $\tau_d/\tau_b=1.05$  implies this defect is a monovacancy. Furthermore, as the sample is p-type with the Fermi level close to the valance band, the  $V_{\text{Sb}}$  vacancy (being a donor) should carry a positive charge and thus is not an effective positron trap. This implies the  $280\text{ps}$  component is another  $V_{\text{Ga}}$ -related defect which becomes abundant after the electron irradiation process. The two  $V_{\text{Ga}}$ -related defects should have different microstructures as they have different positron lifetimes. However, the detail is still unknown and requires further investigation.

## IV. CONCLUSION

Lifetime component  $310\text{ps}$  was identified in the as-grown undoped GaSb sample and it was attributed to the  $V_{\text{Ga}}$ -related defect. Its thermal ionization process ( $0/-$ ) was observed in the

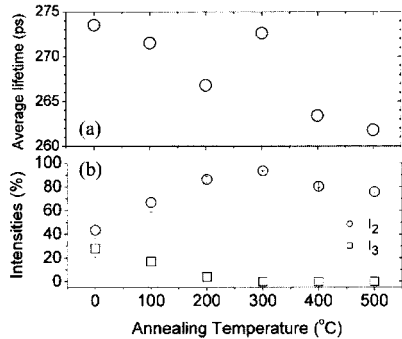


Figure 2 Positron average lifetime, fitted  $I_2$  and  $I_3$  as a function of the annealing temperature for the electron irradiated ( $1.7\text{MeV}$ , dosage of  $10^{16}\text{cm}^{-2}$ ) undoped GaSb sample.

temperature dependent positron lifetime measurements and its ionization energy was found to be  $E(0^-)=83\text{meV}$ . Its concentration was found to be  $5\times 10^{16}\text{cm}^{-3}$  and it is not the residual acceptor of the undoped samples. For the electron irradiated sample, two defect components, namely having lifetimes of 280ps and 315ps, were identified in the as-irradiated sample. The 315ps has very similar characteristic lifetime and annealing behavior (vanishes at  $\sim 300^\circ\text{C}$ ) to the  $V_{\text{Ga}}$ -related found in the non-irradiated samples. The other component 280ps, which was also attributed  $V_{\text{Ga}}$ -related defect, was only found in the electron irradiated sample and thermally stable up to  $500^\circ\text{C}$ .

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