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Gallium vacancy in GaSb studied by positron lifetime spectroscopy and photoluminescence

W. K. Mui, M. K. Lui, C.C. Ling, C. D. Beling, S. Fung
Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China

K. W. Cheah, K. F. Li
Department of Physics, Hong Kong Baptist University, Hong Kong, P. R. China

Y. W. Zhao
P.O. Box 912, Material Science centre, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, P. R. China

E-mail correspondence: ccling@hkucc.hku.hk

ABSTRACT

Positron lifetime technique and photoluminescence (PL) were employed to study the vacancy type defects in *p*-type Zn-doped and undoped GaSb samples. In the positron lifetime study, Ga vacancy related defect was identified in these materials and it was found to anneal out at temperature of about 350°C. For the PL measurement on the as-grown undoped sample performed at 10K, a transition peak having a photon energy of about 777meV was observed. This transition peak was observed to disappear after a 400°C annealing. Our results is consistent with the general belief that the 777meV transition is related to the $V_{Ga}Ga_{Sb}$ defect, which is the proposed residual acceptor of GaSb.

INTRODUCTION

Gallium Antimonide is a III-V semiconductor having a narrow band gap, a small effective electron mass and a high electron mobility. It is the basic material for a variety of lattice-matched materials having band gap ranging from 0.8 to 4.3μm. It is the potential material for fabricating optoelectronic, photovoltaic and high frequency devices. Undoped GaSb is *p*-type and has a hole concentration of 10^{16}-10^{17}cm^{-3} [1,2]. The residual acceptor was known to be doubly ionized [3] and related to a deficiency of Sb or an excess of Ga [4-6]. Annealing the undoped GaSb for several hours converted its *p*-type conducting nature to *n*-type. It was explained by the creation of V_{Sb} upon the annealing, for which V_{Sb} was a donor compensating the residual acceptor. However, if the sample was annealed for several tens of hours, it would convert back to *p*-type with an even larger hole concentration as compared to the original as-grown value [7]. The residual acceptor has long time been attributed to the $V_{Ga}Ga_{Sb}$ defect [7-9]. The increase of hole concentration upon prolonged annealing can be understood by the formation of $V_{Ga}Ga_{Sb}$ resulting from the reaction between the V_{Sb} defect and its neighboring Ga atom. The $V_{Ga}Ga_{Sb}$ defect was also related to a luminescence signal called band *A* (located at about

777meV) which was commonly found in the photoluminescence and cathodoluminecense spectra of a variety of GaSb materials [7,10-15]. However, these correlations between the residual acceptor, the $V_{Ga}Ga_{Sb}$ and the 777meV luminescence signal have not yet been directly confirmed by experimental observation.

Positron lifetime technique is a non-destructive defect probe which is selectively sensitive towards open volume defects [16, 17]. Positrons implanted into a solid will be rapidly thermalized and then undergo diffusion. An open volume defect in the lattice which presents as a potential well, may thus trap the diffusing positrons. The trapping process is indeed a positron state transition from the delocalized Bloch state to the localized defect state. As positrons annihilating at different states have different characteristic lifetime values, defect can thus be identified by its own characteristic lifetime after decomposing the positron lifetime spectrum. Defect information such as the concentration, the microstructure, the charge state and the ionization energy are possibly determined with the use of positron lifetime technique [16,17].

In this study, we have performed annealing studies on the undoped and the Zn-doped GaSb samples with the use of the positron lifetime and the PL techniques with an aim to investigate the correlation between the 777meV luminescence peak and the Ga vacancy positron lifetime signal.

EXPERIMENTAL

8mm×8mm samples were cut from the LEC grown GaSb wafers purchased from the MCP Wafer Technology Ltd., U.K. The thickness of the samples is 0.5mm. Two undoped samples [GaSb042Un and GaSb342Un] cut from two different ingots and one Zn-doped sample [GaSb098Zn] were investigated in the present study. The hole concentrations of the samples obtained by Hall Measurement performed at room temperature were : p[GaSb042Un]=2.5×10^{17}cm^{-3}, p[GaSb342Un]=2.0×10^{17}cm^{-3} and p[GaSb098Zn]=3.3×10^{18}cm^{-3}. The samples were degreased with acetone and ethanol, and then rinsed by deionized water. Isochronal annealing was performed in a nitrogen-hydrogen (80%-20%) forming gas atmosphere. After the 30 minute annealing, the samples were retreated out of the furnace's hot region but still kept in the forming gas atmosphere before they were cooled down.

The positron source used was 30μCi ^{22}NaCl radioactive source encapsulated with kapton foil. The positron source was then sandwiched by the pair of the samples being measured. The positron lifetime spectrometer used in the present study has a resolution of fwhm=235ps. The positron lifetime measurements were carried out at the room temperature and in darkness. Each of the lifetime spectra contained 4 million counts.

In the PL measurements, the samples were excited by the 512 nm line of an argon laser, with typical power of 500 mW, and the excitation light was modulated at 20 Hz using a mechanical chopper. The emitted light was collected and separated by a 0.25 m focal length double monochromator, with slit width of 0.4 mm for both input and output slit, and a 800 nm long-pass filter was used to avoid any second-order light reaching the detector. A liquid nitrogen cooled InSb IR-detector converted the emitted light into electric signal, which was detected using a lock-in amplifier and was recorded with a microcomputer. All measurements were done at 10K, with the samples mounted in an Oxford Instrument closed-cycle He cryostat.

RESULTS AND ANALYSIS

Results of positron lifetime measurements

Room temperature positron lifetime measurements were performed on the samples annealed at different temperatures up to 580°C. The lifetime spectrum is the linear combination of the exponential terms contributed from the corresponding annihilating sites [16,17], i.e.

$$S(t) = \sum_i I_i \exp(-t/\tau_i) \qquad (1)$$

where τ_i and I_i are respectively the characteristic lifetime and the intensity of the *i-th* positron trapping defect. The average lifetime of the positron lifetime spectrum is given by [16,17] :

$$\tau_{ave} = \sum_i I_i \tau_i = \int S(t) t dt \Big/ \int S(t) dt \qquad (2)$$

The average positron lifetime of each of the positron lifetime spectrum annealed at different temperatures were calculated with the results shown in figure 1. For the as-grown Zn-doped sample, the average lifetime τ_{ave} was found to be 274ps. The average lifetime did not vary up to an annealing temperature of 300-400°C, at which it decreased to values of about 272ps. Afterthen, the average lifetime further decreased to about 266ps at an annealing temperature of 580°C. Ling *et al* [18] have analyzed the positron lifetime spectra of this Zn-doped sample and gave the following conclusion. The bulk lifetime of the GaSb was found to be 267±1ps. A two lifetime component fit was found to give good representation to the spectra of the Zn-doped sample at all the annealing temperatures. At annealing temperatures lower than 300°C, the characteristic lifetime of the long lifetime component is constant at about 316±8ps and its intensity is also roughly constant between 50-60%. This 316ps component was attributed to positron annihilating at V_{Ga} related defect. At annealing temperatures ranging between 300° to 400°C, the characteristic lifetime of the defect component was found to increase to 368ps and the defect component intensity decreased to about 15%. This increase of lifetime value and decrease of intensity were attributed to the anneal out of the original V_{Ga}-related and the formation of a new defect *D* having a lifetime of 368ps. This new defect *D* was found to anneal out at 580°C where the defect component intensity decreased to effectively zero.

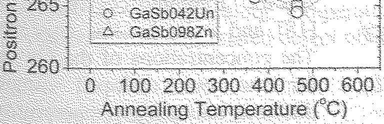

Figure 1 Positron average lifetime as a function of the annealing temperature for the three GaSb samples. The lines joining the data points are only for visual guidance.

For the case of the two undoped samples, their annealing behaviors are very similar. The two undoped samples have average lifetime values higher than the bulk. This implies that there are positron trapping centres in the samples. Unlike the Zn-doped sample which has two annealing stages (namely at 300-400°C and 580°C), there is only one annealing stage at 350°C for the undoped samples. As the 350°C annealing stage in the Zn-doped sample was related to the annealing out of the V_{Ga}-related defect, it is plausible to assign the 350°C annealing observed in the undoped GaSb sample to the same process. As compared to the Zn-doped sample having an average lifetime equal to 272ps after the 350°C annealing, the average lifetime of the undoped samples reaches value of about 266ps, which is the bulk lifetime of GaSb and thus implies no positron trapping centre exists in the undoped samples after the 350°C annealing. This indicates the formation of the defect *D* upon the annealing out of the V_{Ga}-related defect in the Zn-doped sample possibly involves the reaction between the V_{Ga}-related defect and the Zn dopant.

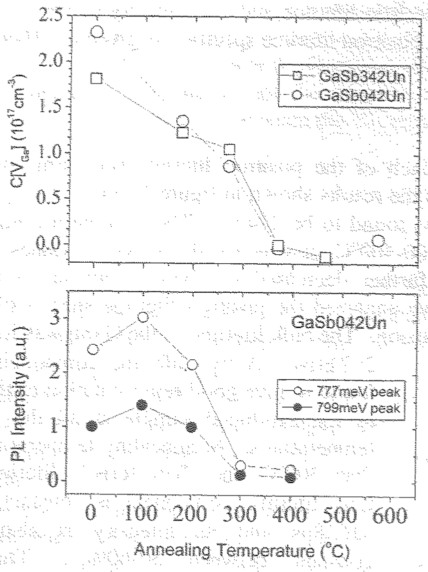

Figure 2. (a) The concentrations of the Ga vacancy related defect for the two undoped samples as a function of the annealing temperature. (b) The PL intensities of the two PL peaks (777meV and 799meV respectively) found in the undoped sample GaSb042Un as a function of the annealing temperature.

As for the undoped samples in which the defect V_{Ga} being annealed out with no formation of new defect, the simple trapping model can be used to describe the positron trapping annihilation in the sample system. The positron trapping rate κ into the Ga vacancy is given by the equation [17]:

$$\kappa = \frac{\tau_{ave} - \tau_b}{\tau_D - \tau_{ave}} \frac{1}{\tau_b} = \mu c \qquad (3)$$

where τ_b=266ps is the bulk lifetime of GaSb, τ_D=317ps is the characteristic lifetime of V_{Ga} [18], $\mu=2\times10^{14} s^{-1}$ is the specific trapping coefficient of V_{Ga} [18] and c is the V_{Ga} concentration. The concentrations of the Ga vacancy for the two undoped samples at different annealing temperatures were calculated and shown in figure 2(a). The Ga vacancy concentrations in the two as-grown undoped samples were found to be about $2\times10^{17}\,cm^{-3}$ and then dropped to nearly zero at the annealing temperature of about 350°C.

Results of PL measurements

Low temperature (10K) PL measurements have been performed on the GaSb042Un undoped samples annealed at different temperatures. Two typical PL spectra, namely those of the as-grown and the 400°C annealed samples, are shown in figure 3. For both of the spectra, the dominant luminescence signals are the peak located at about 777meV. Another two emission signals were also identified at positions of about 760meV (the low energy shoulder of the 777meV dominant emission) and 800meV. The intensities of all the peaks were found to reduce significantly after the 400°C annealing. The PL spectra taken at different annealing temperatures were fitted with the model consisting of three Gaussians. The fitted peak positions were found to be annealing temperature independent for the two stronger signals, namely at 777.36 ± 0.74meV and 798.76 ± 1.70meV respectively. The weak signal at about 760meV was too weak to obtain reliable fitting parameters.

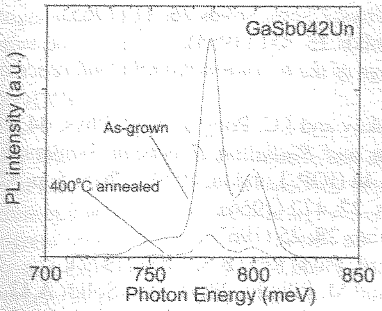

Figure 3 PL spectra of the as-grown and 400°C annealed GaSb042Un undoped GaSb samples. The measurements were performed at T=10K.

The 777meV luminescence signal was found in most of the GaSb materials grown by various methods. It was related to Sb deficiency and was attributed to donor or conduction band to $V_{Ga}Ga_{Sb}$ transition [7,9,11-13]. The 799meV signal observed in the present study is close to the previous observations of PL signals attributed to exciton bound to neutral acceptor $(V_{Ga}Ga_{Sb})^0$ (792-805meV [11-13]). The intensities of the 777meV and 799meV PL signals as a function of the annealing temperature are shown in figure 2(b). From the figure, their annealing behaviors followed the identical trend and thus the two transition would involve an identical defect. This further supports the assignments of the 777meV and the 799meV signals to transitions involving the same defect $V_{Ga}Ga_{Sb}$. Furthermore, as shown in figure 2, the intensities of the two PL peaks significantly reduce at the annealing temperature of 300°C, which is coincident with the annealing temperature of V_{Ga} related defect obtained from the positron lifetime measurements.

CONCLUSION

Positron lifetime and photoluminescence measurements were employed to study the Ga vacancy related defects in Zn-doped and undoped GaSb. By the positron lifetime technique, Ga vacancy was identified in both the Zn-doped and the undoped samples. Two luminescence signals, namely 777meV and 799meV, were identified in the PL measurement and were related to conduction band or donor to $V_{Ga}Ga_{Sb}$ transition and exiton bound with neutral $V_{Ga}Ga_{Sb}$ respectively. The two PL signals and also the positron lifetime Ga vacancy signal disappeared at the annealing temperature of 300°C. This observation is consistent with the general viewpoint that the 777meV and the 799meV PL peaks are related to the $V_{Ga}Ga_{Sb}$ defect.

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