Segercrantz, N.; Slotte, J.; Tuomisto, F.; Mizohata, K.; Raisanen, J.

Instability of the Sb vacancy in GaSb

Published in:
Physical Review B

DOI:
10.1103/PhysRevB.95.184103

Published: 03/05/2017

Please cite the original version:

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Instability of the Sb vacancy in GaSb

N. Segercrantz,* J. Slotte, and F. Tuomisto
Department of Applied Physics, Aalto University School of Science, P.O. Box 15100, FIN-00076 Aalto, Finland

K. Mizohata and J. Räisänen
Department of Physics, University of Helsinki, P.O. Box 43, FI-00014 University of Helsinki, Finland

(Received 18 November 2016; revised manuscript received 30 March 2017; published 3 May 2017)

We demonstrate that the instability of the Sb vacancy in GaSb leads to a further increase in the acceptor-type defect concentration in proton irradiated undoped, p-type GaSb. Using positron annihilation spectroscopy in situ with 10 MeV proton irradiation at 35 K, we find that the irradiation produces both native vacancy defects in GaSb. However, the Sb vacancy is unstable above temperatures of 150 K and undergoes a transition resulting in a Ga vacancy and a Ga antisite. The activation energy of this transition is determined to be 0.6 eV ± 0.1 eV. Our results are in line with the established amphoteric defect model and prove that the instability of the Sb vacancy in GaSb has a profound role on the native defect concentration in GaSb.

DOI: 10.1103/PhysRevB.95.184103

I. INTRODUCTION

GaSb is a narrow-gap compound semiconductor with applications in high speed electronics, thermoelectrics, and long-wavelength optoelectronics. It exhibits uniquely high asymmetry in its mass transport properties: self-diffusion experiments have revealed that Ga atoms diffuse three orders of magnitude faster through the lattice than Sb [1]. Compared to self-diffusion in elemental semiconductors [2,3] and other binary III-V compounds [4–7], the diffusivity of Sb in GaSb near the melting point is several orders of magnitude lower. The explanation for the unusual behavior has been suggested to lie in the native defect distribution. The Sb vacancy has been proposed to be unstable, easily exchanging sites with a neighboring Ga atom, resulting in a Ga vacancy (V_{Ga}) and a Ga antisite (Ga_{Sb}). This mechanism would enhance the Ga diffusion while at the same time suppressing the diffusivity of Sb due to the lack of Sb-related defects in the lattice.

Another unusual asymmetry in GaSb is its strong propensity towards p-type conductivity. This type of behavior can be explained as originating from the position of the valence and conduction band edges relative to the Fermi level stabilization energy (E_{FS}) [8]. In GaSb, the valence band essentially coincides with this level, favoring the equilibrium formation of acceptor-type defects [9]. Further, this may lead to an amphoteric nature of charged defects introduced through nonequilibrium processes, as observed in, e.g., GaAs and InN [8,10].

The identity of the acceptor-type defect responsible for the p-type conductivity of nominally undoped GaSb has been under debate for quite some time [11–22]. Most recent experimental and theoretical work show that V_{Ga} and G_{Sb} are the dominant acceptor-type native defects in GaSb [17,21–23], but their relative importance depends on the crystallization conditions [21–23]. For Czochralski-grown bulk GaSb crystals the concentration of Ga antisites is an order of magnitude higher than that of the Ga vacancies, making the antisite the main cause for p-type behavior. In epitaxial GaSb the Ga vacancies play a more significant role.

In this work, we reveal the unstable behavior of the Sb vacancy by irradiating undoped, p-type GaSb with high-energy protons and performing positron annihilation spectroscopy both ex situ and in situ and subsequently annealing the material in the temperature interval 35–300 K. Both Ga and Sb vacancy defects are introduced in the lattice by irradiation at low temperature. At a temperature of approximately 150 K, the Sb vacancy becomes unstable, undergoing a transition resulting in a Ga antisite and a Ga vacancy thereby increasing the acceptor-type defect concentration in GaSb. Our results show that the instability of the Sb vacancy has a clear effect on the native defect distribution in GaSb.

II. EXPERIMENTAL DETAILS

The studied material consists of undoped, Czochralski-grown, p-type GaSb with [Ga_{Sb}] ≈ 10^{17} cm^{-3} and [V_{Ga}] ≈ 10^{16} cm^{-3} [22]. Positron annihilation spectroscopy is a nondestructive technique especially suitable for studying open-volume defects and negatively charged ions [24]. The positron experiences the absence of a nucleus as a potential well where the antiparticle can get trapped before annihilation. Negative ions can also trap positrons in hydrogen-like Rydberg states. The positron lifetime gives information on the positron trapping states in the crystal. Due to the reduced electron density at vacancy defects, the positron lifetimes are longer compared to the lifetimes of positrons annihilating in a delocalized state in the lattice. Negative ion-like defects produce a lifetime similar to that of the delocalized state in the lattice.

In our experiments, the GaSb samples were mounted in a sandwich setup with the source wrapped in a micrometer thick Al foil, on a copper sample holder in thermal contact with a closed cycle helium cryostat. We used a conventional fast-fast coincidence system with Gaussian timing resolution of 260 ps (FWHM) and a 20 μCi 22NaCl source for the positron lifetime experiments. Prior to analysis, the positron annihilation in the source, in the Al foil, and as positronium were subtracted from the lifetime data. For the irradiation, a
sample holder with an aperture of approximately 30 mm$^2$ was used. The irradiations were performed with 10 MeV protons with a projected range of 400 μm in GaSb. The sample facing the ion beam was mechanically ground to 250 μm leading to a projected range of approximately 150 μm in the second sample in the sample-source-sample sandwich. This depth is sufficient to avoid end of range effects, as the mean implantation depth of positrons is 33 μm in GaSb. This experimental procedure has been shown to be efficient in producing monovacancy defects, without evidence of larger clusters, in Si and Ge [25,26].

Two different irradiation experiments were carried out. Positron lifetime measurements were performed ex situ on GaSb samples irradiated at room temperature (RT) with fluences in the range $5 \times 10^{12}$−$1 \times 10^{15}$ cm$^{-2}$. The flux was kept constant throughout the irradiations. Based on these measurements, the fluences of $1 \times 10^{14}$ and $7 \times 10^{14}$ cm$^{-2}$ were used for samples irradiated at 35 K and subsequently thermally annealed while performing in situ positron measurements. The annealing was done for 30 min from 35 K to RT with steps of 20 K and with measurements performed at 35 K between the annealing steps. In order to avoid any unwanted background in the positron data from proton-reaction-induced decaying Ge and Te isotopes created during the irradiation, the samples were kept at the irradiation conditions for approximately four days before performing the positron measurements.

Rutherford backscattering spectrometry (RBS) in channeling geometry was performed on samples irradiated with fluences in the range $5 \times 10^{14}$ cm$^{-2}$−$1 \times 10^{15}$ cm$^{-2}$. The measurements were done using $^4$He$^{2+}$ particles with an energy of 1 MeV. The result shows that the samples remain crystalline during irradiation. In Fig. 1, the result for the sample irradiated with the fluence of $1 \times 10^{15}$ cm$^{-2}$ is shown.

III. RESULTS

Figure 2 shows the results of the ex situ measurements of the average positron lifetime ($\tau_{ave}$) as a function of irradiation fluence. All the experiments were performed at RT. The average positron lifetime in as-grown GaSb is shown for comparison. As-grown, undoped GaSb is $p$-type and therefore not defect-free, since abundant concentrations of positron trapping, acceptor-type defects are present in the material [22]. As can be seen in the figure, fluences of $5 \times 10^{13}$ cm$^{-2}$ or higher are needed for a detectable change to be observed in the lifetime data. Further increasing the fluence increases the $\tau_{ave}$ compared to that of the as-grown material. An increase in $\tau_{ave}$ is a sign of enhanced positron trapping at vacancy defects.

The in situ measurements of $\tau_{ave}$ as a function of annealing temperature are shown in Fig. 3. The irradiation as well as the positron lifetime measurements were performed at 35 K. At this temperature, $\tau_{ave}$ in as-grown GaSb was measured to be 257 ps, 5 ps shorter than at RT, in agreement with earlier results [20]. In the as-irradiated samples, $\tau_{ave}$ is clearly longer than that of as-grown GaSb, confirming vacancy formation as a result of the irradiation performed at the low temperature. A clear effect of the annealing can be seen in the data for the sample irradiated with the fluence of $7 \times 10^{14}$ cm$^{-2}$ (hereafter called high fluence). Upon annealing, $\tau_{ave}$ remains constant up to temperatures of approximately 150 K, above which there is an abrupt drop. Increasing the annealing temperature further does not affect $\tau_{ave}$. Annealing has no noticeable effect on $\tau_{ave}$ in the sample irradiated with the fluence of $1 \times 10^{14}$ cm$^{-2}$ (hereafter called low fluence). In both irradiated samples, $\tau_{ave}$ is higher after annealing than it is in as-grown GaSb indicating a permanent increase in the vacancy defect concentrations as a result of the irradiation.

In previous studies, the positron lifetime at different vacancy-type defects in GaSb has been estimated both experimentally [22] and computationally [23]. An experimental positron lifetime of $\tau_{V_{Ga}} = 285$ ps was estimated for the $V_{Ga}$, an increase of 40 ps compared to the estimated bulk lifetime of $\tau_{b} = 245$ ps. For the neutral $V_{Sb}$, DFT calculations suggest...
a positron lifetime 33 ps longer than that of the neutral $V_{Ga}$ corresponding to a lifetime of $\tau_{V_{Ga}} = 320$ ps in the vacancy (no experimental values exist for the Sb vacancy).

The positron lifetime spectrum is a sum of exponentially decaying components of the form $e^{-\lambda t}$, where $\lambda_i = \frac{1}{\tau_i}$ is the positron annihilation rate in state $i$ and $t$ is the measured time. One of the components is the so-called reduced bulk lifetime [24]. The lifetime components can usually be decomposed successfully when the positron lifetimes in the different trapping states are well separated; $\frac{\tau_i}{\tau_{V_{Ga}}} = 1.3–1.5$ [24]. If the spectrum consists of three or more components, or if the lifetimes of the components are too close, decomposing becomes more difficult or impossible. Figure 4 shows the positron lifetime spectra of the high fluence sample annealed at different temperatures. The steepness of the spectra are different indicating a longer average positron lifetime after the 50 K annealing compared to the 290 K annealing. Both measured spectra display a linear behavior. Hence positron lifetimes in different defects acting as traps in the studied samples cannot be reliably separated from the measured data.

IV. DISCUSSION

We first consider the effect of the irradiation on the GaSb lattice. The range of the fluences used for the irradiations is sufficient to produce point defects, however not high enough for extended damage to be created in the lattice. This is confirmed by the channeling results showing unaltered crystallinity and is in line with earlier studies of irradiated Si and Ge using similar fluences [25,26]. The point defects produced in these conditions are primarily vacancies and interstitials on both sublattices. As positrons are sensitive to vacancies but not to interstitials, it is sufficient to consider only vacancies in the following.

For the irradiation performed at low temperature, the magnitude of the high and low fluences used is of the same order; therefore, only a quantitative difference in the point defect production is expected. In order for the measured drop in $\tau_{ave}$ to emerge with increasing fluence, the concentration of the defects in question and the associated positron trapping rate $\kappa$ have to overcome that of the pre-existing acceptor-type defects and of the other defects produced in the irradiation. In CZ-grown, as-grown, $p$-type GaSb both Ga vacancies and Ga antisites are abundantly present and act as positron trapping defects [22]. Hence the defect causing the annealing effect must have a higher production rate than the other defects. The production rates of the primary defects in GaSb can be estimated using the displacement cross section $\sigma$ as described in Ref. [27]. By averaging $\sigma$ in the range 1–10 MeV and using the displacement energies for Ga and Sb from Ref. [28], the production rates are obtained as 930 cm$^{-1}$ and 670 cm$^{-1}$ for Sb and Ga vacancies, respectively. Thus irradiation creates primarily 40% more Sb than Ga vacancies in GaSb. This would imply that the simplest interpretation for the observed difference between the low and the high fluence is that both Ga and Sb vacancies are observed at low temperature but that the Sb vacancies disappear irreversibly at temperatures above 150 K.

To check for the viability of this interpretation, we estimate the positron annihilation fractions at vacancy defects produced by irradiation at 35 K in the as-irradiated samples. The measured average lifetime is the sum of the positron lifetimes in different states weighted by the positron annihilation fractions: $\tau_{ave} = \eta_B \tau_B + \sum_i \eta_i \tau_i$ and $\eta_B + \sum_i \eta_i = 1$. The fraction $\eta_D$ of positrons annihilating as trapped at a defect D is [29]

$$\eta_D = \frac{\kappa_D}{\lambda_B + \sum_i \kappa_i},$$

where $\kappa_i$ denotes the trapping rate to a state $i$ and $\lambda_B = \frac{1}{\tau_B}$ is the annihilation rate of free positrons in the lattice. The trapping rate to a defect is given by $\kappa_D = \mu_D[D]/N_A$, where $[D]$ denotes the defect concentration and $N_A$ the atomic density of the lattice. The trapping coefficient $\mu_D$ depends on
the charge of the defect. The Sb vacancies are predicted to be neutral, whereas a large fraction of the Ga vacancies and the Ga antisites are negatively charged [17,22]. For neutral vacancies in semiconductors, the temperature independent trapping coefficient is \( \mu_D \approx 1 \times 10^{13} \text{ s}^{-1} \). This is a factor of two lower than that for negatively charged vacancies at RT, that in addition displays a \( T^{-1/2} \) temperature dependence [29]. The trapping fraction into negatively charged Ga vacancies is given by

\[
\eta_{V_{Ga}} = \frac{\kappa_{V_{Ga,\text{ irr}}} + \kappa_{V_{Ga,\text{ irr}}} + \kappa_{GaSb,\text{ irr}} + \kappa_{V_{Ga,\text{ irr}}}}{\lambda_B + \kappa_{V_{Ga,\text{ irr}}} + \kappa_{V_{Ga,\text{ irr}}} + \kappa_{GaSb,\text{ irr}} + \kappa_{V_{Ga,\text{ irr}}}}.
\]

(2)

and the trapping fraction into neutral Sb vacancies is given by

\[
\eta_{V_{Sb}} = \frac{\kappa_{V_{Sb,\text{ irr}}} + \kappa_{V_{Sb,\text{ irr}}} + \kappa_{GaSb,\text{ irr}} + \kappa_{V_{Sb,\text{ irr}}}}{\lambda_B + \kappa_{V_{Sb,\text{ irr}}} + \kappa_{V_{Sb,\text{ irr}}} + \kappa_{GaSb,\text{ irr}} + \kappa_{V_{Sb,\text{ irr}}}}.
\]

(3)

\( \kappa_{V_{Ga,\text{ irr}}} \) and \( \kappa_{GaSb,\text{ irr}} \) denote the trapping rates into Ga vacancies and Ga antisites in as-grown GaSb, respectively. The trapping fraction into Sb vacancies and Ga vacancies created in the irradiation are denoted by \( \kappa_{V_{Sb,\text{ irr}}} \) and \( \kappa_{V_{Ga,\text{ irr}}} \), respectively.

Using the information above, positron annihilation fractions of \( \sim 6\% \) and \( \sim 33\% \) are estimated for the Sb and Ga vacancy in the low fluence sample, respectively. The large fraction of positrons annihilating as trapped to Ga vacancies indicates that any change occurring to this defect should be easily detectable in the measurement. On the other hand, the fraction of positrons annihilating as trapped at Sb vacancies is low enough for their possible recovery at 150 K not to be visible. In the high fluence case, the annihilation fractions for the Sb and Ga vacancies are estimated as \( \sim 16\% \) and \( \sim 66\% \), respectively. The fraction of positrons annihilating as trapped at Sb vacancies is clearly high enough in this case to explain the observed annealing temperature dependence in the positron lifetime. The slightly higher \( \tau_{ave} \) measured in the low fluence sample after annealing compared to that in the high fluence sample is related to charge states of the defects, as the trapping coefficient is higher for negative defects compared to neutral ones. Defects produced in the irradiation affect the Fermi level position in the band gap, which in turn has a large impact on the relative concentrations of negative and neutral defects.

Assuming that the effect seen in the data at 150 K is the suggested transition [1],

\[
Ga_{Ga} + V_{Sb} \rightarrow V_{Ga} + Ga_{Sb},
\]

(4)

and assuming that this is the only way for the \( V_{Sb} \) to disappear, we can estimate the total concentrations of \( V_{Ga} \) and \( Ga_{Ga} \) in GaSb at RT. In the reaction, \( Ga_{Ga} \) denotes a Ga atom on its own sublattice. Using the above described relations and the estimated lifetimes \( \tau_G = \tau_{Ga} = 245 \text{ ps} \) and \( \tau_{V_{Ga}} = 285 \text{ ps} \) in the bulk, Ga antisite and Ga vacancy [22], the average positron lifetime can be estimated as a function of fluence as shown in Fig. 2 (black dotted line). For comparison, the average positron lifetime is also estimated based on positrons annihilating at pre-existing defects and in Ga vacancies created by irradiation and shown (orange dashed line) in the same figure. The latter model saturates at high fluences to 285 ps corresponding to the positron lifetime in \( V_{Ga} \). The model not taking into account the transition of the Sb vacancy further increasing the concentration of acceptor-type defects clearly overestimates the \( \tau_{ave} \) at higher fluences and does not explain the measured data.

We can fit an activation energy to the measured \( \tau_{ave} \) as a function of annealing temperature as in Ref. [30] for the sample irradiated with the high fluence. The isochronal annealing process can be described as [27]

\[
[D]_{i+1} = [D]_i + ([D]_i - [D]_\infty) \exp[\nu t \exp[-E_A/k_BT_i]],
\]

(5)

where \( i \) denotes the annealing step, the temperature range is \( T_0 = 35 \text{ K} \) and \( T_{i+1} = (50 + 10i) \text{ K} \), \( t = 1800 \text{ s} \) is the annealing time, \( \nu = 10^{13} \text{ s}^{-1} \) is the frequency factor assumed to be constant, and \( [D]_\infty \) is the decreased defect concentration due to the annealing. The fit based on Eq. (5) is shown in Fig. 3 and gives the activation energy \( E_A = 0.6 \pm 0.1 \text{ eV} \). This is the energy barrier for the process (4) describing the transition of the Sb vacancy to two acceptor-type defects. The value is comparable to the migration energy of 0.32 eV for the highly unstable Si vacancy in \( p \)-type Si [31].

In Fig. 5, measurements of \( \tau_{ave} \) at 35 K and at RT for as-grown GaSb and for the sample irradiated with the high fluence are illustrated. The arrow indicates the order of the post-growth treatments performed on the irradiated sample. At both low temperature and RT, \( \tau_{ave} \) in the irradiated sample is higher compared to the as-grown GaSb indicating an increased Ga vacancy concentration as a result of the irradiation. Increasing the measurement temperature increases \( \tau_{ave} \) both annealed samples. At low temperatures, Ga antisites have been shown to effectively compete in positron trapping with Ga vacancies resulting in the 5 ps decrease in \( \tau_{ave} \) in as-grown GaSb [22]. For the irradiated sample, the decrease in \( \tau_{ave} \) is larger that that of the as-grown GaSb, indicating that the Ga antisite concentration also increased in the irradiation. The increase in the acceptor-type defect concentration of irradiated GaSb and the instability of the Sb vacancy are in good agreement with the high-lying bands strongly favoring acceptor-type defects.
defects formation [8]. The phenomenon is strong enough to cause amphoteric instability of donor-type defects such as the Sb vacancy.

V. CONCLUSIONS

In conclusion, we have shown that the Sb vacancy in GaSb becomes unstable at temperatures above 150 K and undergoes a transition resulting in a Ga antisite and Ga vacancy. The Sb vacancy activation energy is estimated to be $0.6 \pm 0.1\,\text{eV}$, which is comparable to that of the unstable Si vacancy in Si. The experiments were performed by irradiated undoped, $p$-type GaSb with high-energy protons and using positron annihilation spectroscopy ex situ as well as in situ and subsequently annealing the samples. Due to the instability of the Sb vacancy, the acceptor-type defect concentration in $p$-type GaSb is further increased as a result of irradiation. Our results are in agreement with the findings of self-diffusion experiments in GaSb.

ACKNOWLEDGMENT

We gratefully acknowledge Jukka Viheriälä for performing the mechanical grinding on the GaSb samples.