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Proton irradiation-induced defects in undoped GaSb studied by positron lifetime spectroscopy and photoluminescence

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Undoped GaSb was irradiated by 2.6 MeV protons. The irradiation-induced defects were studied by positron lifetime spectroscopy (PLS) and photoluminescence (PL). Positron lifetime measurements showed that vacancy-type defects were introduced after irradiation, and divacancies were formed at higher irradiation dose. Annealing experiments revealed there were different annealing steps between the as grown and proton-irradiated samples, the reason for which was tentatively attributed to the formation of divacancies in the proton-irradiated samples during annealing. All the vacancy defects could be annealed out at around 500 ^{o}C. The PL intensity quickly fell down after proton irradiation and decreased with increasing irradiation dose, indicating that irradiation induced non-irradiative recombination centers, whose candidates were assigned to the vacancy defects induced by proton irradiation.

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1. Introduction

Gallium antimonide (GaSb) is a III-V semiconductor with a narrow band gap of 0.7 eV at 300 K and 0.81 eV at 2 K, thus making it a particularly suitable candidate for application in long wavelength lasers and low loss optical fiber. Due to its small effective electron mass and high electron mobility. GaSb has great potential application in fabricating high-efficiency optoelectronic devices. Undoped GaSb is always p-type and has a hole concentration ~10^{17} cm^{-3} irrespective of growth techniques and conditions. The residual acceptors is usually associated with native Ga vacancies and antisite defects[1]. From the theory's calculation and experiments [2,3, 4], it is proposed that Ga_{Sb} is the most important defect responsible for p-type conduction.

Defects play a major role in the electrical and optical properties of semiconductor by acting as carrier recombination, scattering centers and traps, therefore understanding the defects properties in the materials is vast important to device fabrication. Irradiation with particles will cause damage to semiconductor materials and more or new type of defects might be introduced by causing atomic displacement or ionization, as a result, leading to the reduction of minority carrier lifetime and the creation of electron-hole pairs. Proton irradiation is a very convenient and commonly used means for device isolation in semiconductor materials [5,6]. Up to now, a great amount of work have been carried out to investigate irradiation-induced defects in semiconductors, however, studies on the defects properties in GaSb are rather scarcer compared in other semiconductors and only limited information is available so far concerning the effect of proton irradiation on the physical properties of GaSb. Therefore, it is necessary and significant to study proton irradiation effects on GaSb.

Positron lifetime spectrometer is a sensitive and effective probe to study the defects in solids[7,8]. Positrons implanted to material are strongly repelled by the positively charged ion cores due to Coulomb repulsion, and could be captured by vacancy-type defect which acts as attractive center since there is a missing atom in the vacancy. Because of the reduced electron density and the missing ion cores in the defects site, the trapped positron lifetime increases. As the positrons trapped in different defects have different positron annihilation rates, the positron lifetime could be used to identify and characterize the defects.

In this paper, defects in undoped GaSb subjected to 2.6 MeV proton irradiation with a dose range from 1×10^{14} cm^{-2} to 3×10^{15} cm^{-2} were studied by positron lifetime spectrometer and photoluminescence

2. Experimental

The undoped GaSb samples of a size $10 \times 10 \times 0.6$ mm^{3} were cut from crystals grown by the liquid-encapsulated Czochralski method. They are (001) orientation with a hole concentration about 1×10^{17} cm^{-3}. The proton irradiation was performed using a 4.5 MeV single-ended electrostatic accelerator in the Key laboratory of heavy ion physics(Beijing University), Ministry of Education. The GaSb samples were irradiated with 2.6 MeV protons having a fluence of 1×10^{14} cm^{-2}, 1×10^{15} cm^{-2} and 3×10^{15} cm^{-2}. Isochronal annealing up to 500 ℃ was performed in nitrogen atmosphere for a period of 30 min. After each annealing step, the samples were still kept in the nitrogen gas atmosphere until they were cooled down to room temperature. The positron lifetime spectra were measured by a conventional fast-fast time coincidence system with a time resolution of 260 ps. The positron source ^{22}Na with an activity 30 µCi was deposited on an aluminium foil and sandwiched between a pair of identically treated samples. Each of the lifetime spectra collected 2.5×10^6 counts. The positron lifetime spectra were analyzed by PATFIT program which fits the spectrum data to the sum of exponential decays after subtracting the background and the source contribution. PL measurements were carried out at 77K using a closed-cycle He refrigerator. The samples were excited by a He–Ne laser at 632.8 nm with a power of 300 mW. The luminescence signal was detected by a liquid N_2-cooled Ge photodetector with lock-in technique.

3. Results and discussion

In this work, we used the program SRIM-2008 which is based on the Monte Carlo method to simulate 2.6 MeV proton irradiation induced defects[9]. The concentration of vacancies produced by irradiation versus sample depth is presented in Fig 1. It is shown that the vacancies have a depth distribution along the proton implantation path. The induced vacancies concentration around the implanted way mainly lies within the range of 10^{-5}~ 10^{-4} (Angstrom / ion) , and the largest concentration of defects is around the end of the range of protons, where the depth is about 52 μm□For every implanted proton, about 26 vacancies are produced according to the simulation result. The positron implantation depth R is calculated by the equation: $R^{-1}=17\rho/E^{1.43}$ (cm^{-1}), where ρ is the GaSb sample density and E is the largest positron energy. We obtained R=43.95μm by taking ρ= 5.619 g/cm^3 and E= 0.545 MeV. This indicates that the vacancies induced by proton irradiation are under the detection area of positron.

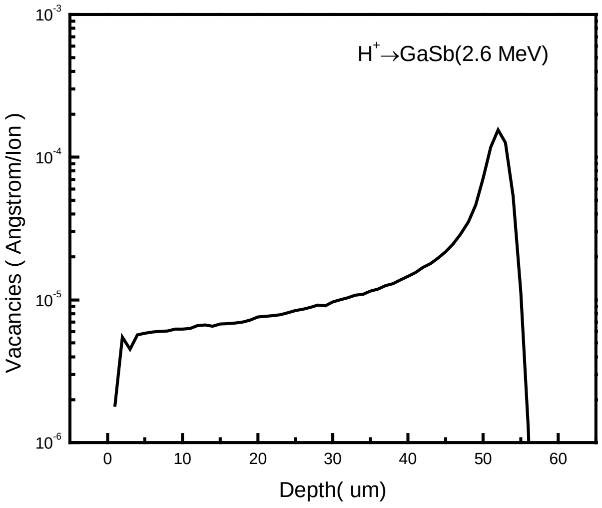


Fig.1. Monte Carlo simulation of the depth distribution of vacancies produced by 2.6 MeV proton irradiation in GaSb.

The samples treatments and positron lifetime results measured at room temperature are listed in Table 1. For all of the GaSb samples, two lifetime components were required to give good fits to the spectra. The positron average lifetime was deduced from

$$\tau_{av}=\tau_1 I_1+\tau_2 I_2 \quad (1)$$

where τ_1 is attributed to positron lifetime of free positrons, the longer lifetime component τ_2 related to positron annihilating in defect, I_1 and I_2 the relevant intensities of positron annihilation. For the as grown sample , we solved out a long lifetime component with about 309 ps, which is in agreement with the results obtained by C C Ling[3,10], where a long lifetime of 315 ps assigned to V_{Ga}-related monovacancy defect was found in as grown undoped GaSb and Zn-doped GaSb. As the theoretical calculation shows that the V_{Sb} is positively charged and V_{Ga} related defect is negatively charged in p-type GaSb[11], we also assume the 309 ps component is V_{Ga}-related defect.

After proton irradiation with a dose of 1×10^{14} cm^{-2}, the positron lifetime changed surprisingly as compared with that in the as grown sample. The defect component lifetime turned out to be 281 ps, and the average lifetime decreased from 261 ps to 258ps. As may be expected , new defects would be introduced after irradiation so that the average lifetime should increase. There are two possibilities responsible for the phenomenon. One might be that a new vacancy-type defect with a smaller positron lifetime(less than 281ps) was introduced after proton irradiation and acted as a competitor with the 309 ps lifetime component in trapping positrons, however, we could not solve it out by decomposing the lifetime spectrum due to difficulty of three lifetime component fit in semiconductors. This explanation agrees with the results found in reference[12], where the average lifetime also slightly decreased after electron irradiation in undoped GaSb and they assumed that it was due to a significant fraction of positron annihilating in the electron irradiation-induced 280 ps positron trapping competitor. Another reason might be that vacancies induced by proton irradiation had been recoveried at room temperature annealing. Yamaguchi has found that the induced defects could be annealed out at room temperature in electron-irradiated InP semiconductor[13]. The recovery of irradiation-induced defects might also happen in the proton-irradiated undoped GaSb sample, resulting in no increase of the positron average lifetime. Which reason would be responsible for the mechanism is still a question and further study is needed to confirm the possibilities.

When increasing the irradiation dose to 1×10^{15} cm^{-2}, the defect concentration increased from 75.74% to 78.33% with only a slight increase of the defect lifetime. Apparently, as can be seen from the table, the positron average lifetime increased to 263 ps, which was a little higher than that in the lower dose irradiation sample, suggesting that more defects were induced upon proton irradiation with higher fluence irradiation.

At the highest irradiation dose of 3×10^{15} cm^{-2}, the second component lifetime increased to 330 ps, which is a typical divacancy defect lifetime with a ratio of τ_2/τ_b ~ 1.31

in GaSb by taking the bulk lifetime as 253 ps[14], indicating that divacancies were formed. It is assumed that the monovancies could form divacancies by diffusing and interacting with other monovacancies at room temperature annealing. The decrease of the defect lifetime intensity gives direct evidence that the monovancies have been annealed out and converted to divacancies after proton irradiation with the highest dose of 3×10^{15} cm^{-2}.

Table 1. Positron lifetime results of 2.6 MeV proton irradiated GaSb

Dose□ion/cm^2□	τ_1 (ps)	τ_2 (ps)	I_2(%)	τ_m (ps)
0	235.9±5.6	309±22	33±20	260.64±0.5
1.0×10^{14}	186.1±6.2	281±4	75.74±7.3	258.22±0.5
1.0×10^{15}	172.1±5.1	288±3.1	78.33±3.98	263.04±0.5
3.0×10^{15}	233.3±7.6	330.7±15.1	30±9.19	262.54±0.5

Because the positron average lifetime has the high statistical accuracy and is independent of decomposition of the spectra, it was utilized to investigate the annealing behavior of proton-irradiation induced defects with temperature range between 50 and 500 □. Fig 2 shows the positron average lifetime as a function of annealing temperature in the as grown GaSb. We could observe that there were two annealing stages and all vacancies could be annealed out at around 500□. From the experiment by A.Poly[15]□a recovery stage below 400 K was observed on study of electron irradiated GaP and assigned this stage to be the annealing of Ga vacancies, thus we believe that the annealing process below 100 □ in undoped GaSb might be also caused by recovery of Ga vacancies. The second annealing step over 350 □ was found in many experiments[10,12], and often attributed to be the annealing of V_{Ga}–related defects. If the annealing stage in 0-100 □ is attributed to the annealing of Ga vacancies, the second annealing stage might result from the annealing of other kind of defects, most likely another kind of Ga vacancies or vacancy complexes which have larger mobile energy.

The annealing behavior in differently proton-irradiated GaSb is presented in fig 3 with irradiation doses of 1×10^{14} cm^{-2},1×10^{15} cm^{-2} and 3×10^{15} cm^{-2} . It is obvious that there are also two annealing steps in the irradiation samples, however, a typical feature of the annealing curves is that the average lifetime first increases instead of having an abrupt drop during the annealing temperature of 50-200□. In reference[16], V.Rank found that divacancies or vacancy complexes were formed in electron irradiated Si doped with different impurities during annealing, resulting in a similar positron average lifetime peak. In electron irradiation on undoped GaSb[12], S K Ma also found that the positron average lifetime first had a slight increase and then decreased during annealing temperature range of 100-300 □, however, no further explanation was made there. After irradiation, many more defects would be introduced into samples. During annealing process, monovacancies could easily diffuse to form divacancies leading to a larger positron average lifetime, thus we believe that the positron average lifetime peaks around 50-200□ in the proton irradiated samples origin from the formation of divacancies. However, it is not clear what kind of divacancy is the candidate from present work. For all the irradiation samples , the positron average lifetime reached the bulk lifetime about 253 ps at around 500 □, indicating all the vacancies induced by irradiation could be annealed out at this temperature.

After proton irradiation, the implanted proton will be left in the material and form the hydrogen impurity by capturing a electron. D Shaw proposed that mobilities of all defects excepting $V_{Ga}Ga_i$ were enhanced in the presence of hydrogen as an impurity in the GaSb lattice[4]. As can be seen from the annealing behavior of proton irradiation samples, the positron average lifetime decreases sharply as compared to the as grown sample. It is most likely that hydrogen impurity has accelerated the annealing process by enhancing the mobilities of V_{Ga} related defects.

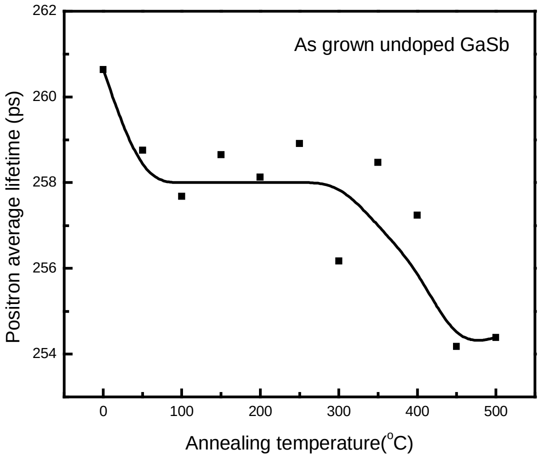
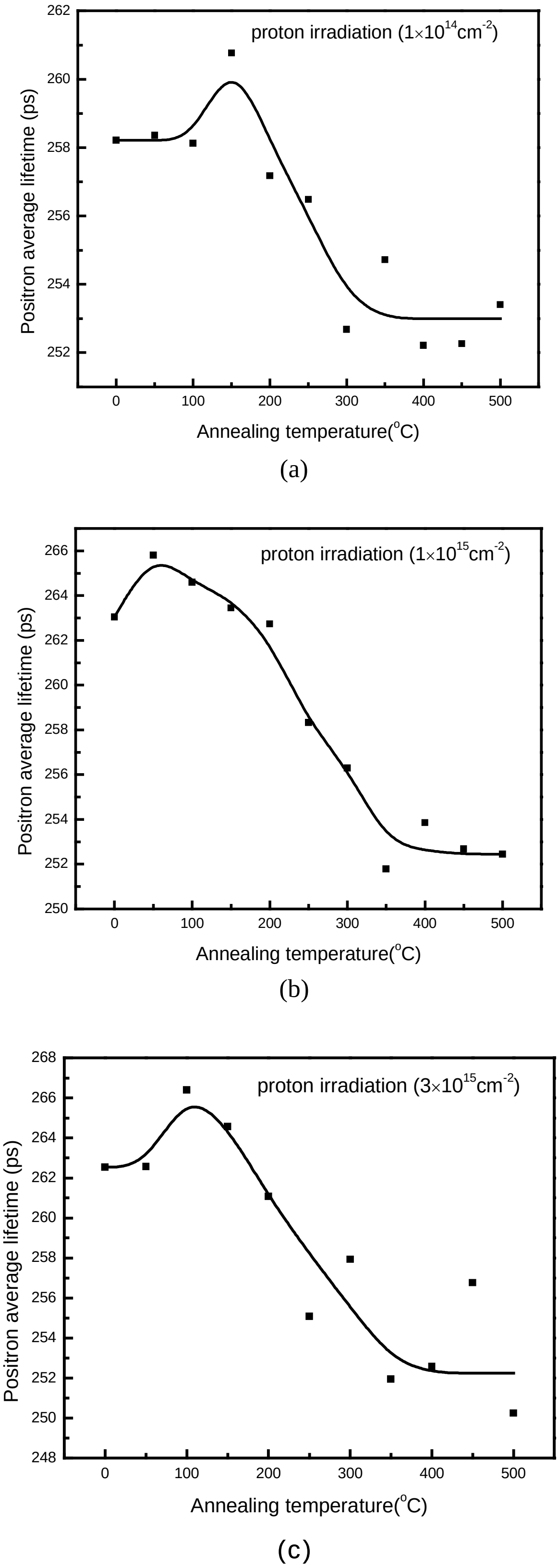


Fig. 2. The positron average lifetime as a function of the annealing temperature in undoped GaSb. Lines are drawn to guide the eyes

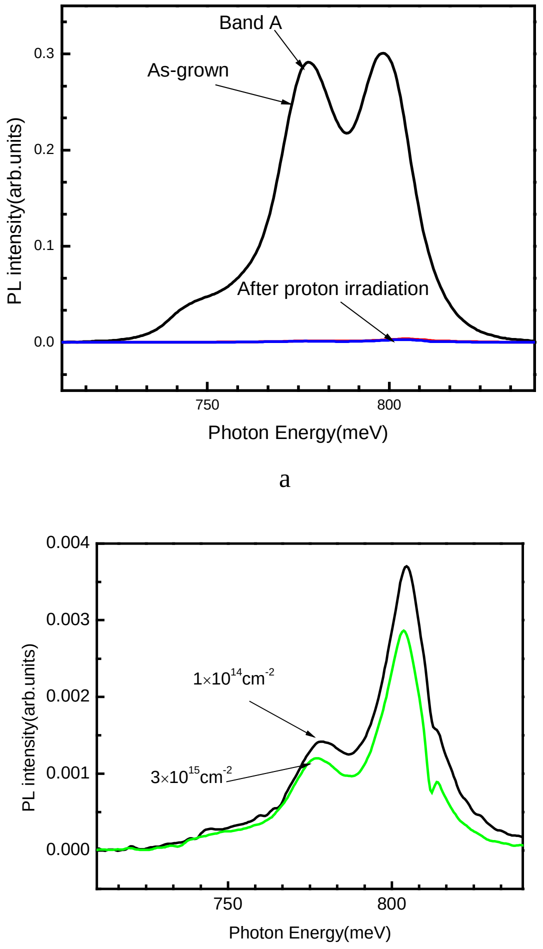


(a)

(b)

(c)

Fig. 3. The positron average lifetime in dependence on the annealing temperature in proton-irradiated gasb with different irradiation doses (a) 1×10^{14} cm^{-2} (b) 1×10^{15} cm^{-2} (c) 3×10^{15} cm^{-2}. Lines are drawn to guide the eyes.



a

b

Fig.4. Photoluminescence spectra of proton irradiatied GaSb with different irradiation doses performed at 77 K

The PL spectra of the as grown and proton irradiated undoped GaSb samples with irradiation doses of 1×10^{14} cm^{-2} and $3\times10^{15}cm^{-2}$ are presented in fig 4. It is clear that in the as grown sample there are two main peaks located at the position of 777 meV and 799 meV, which are attributed to the conduction band or donor to $V_{Ga}Ga_{Sb}$ transition (called band A) and the exciton bound to $V_{Ga}Ga_{Sb}$ (known as BE_4)respectively [17,18]. Another peak with a much weak intensity at 744 meV corresponds to the LO phonon replica of band A. After proton irradiation their intensities quickly fall down and become negligible. For detailed analysis on proton irradiation effect we draw again the PL spectra of proton-irradiated samples with an enlarged range in fig 4 (b). It is shown that the PL spectra still contain two peaks with much lower intensities, and the peaks' intensities decrease with increasing the irradiation dosage, which is known as PL quenching. This phenomenon has also been observed by S.K.Ma in electron irradiated GaSb[12], where the PL intensity as a function of the irradiation dosage behaviored in a similar way. The PL quenching in the electron irradiated GaSb is much more moderate and only after a high irradiation dose of 10^{17}cm^{-2} the emission practically disappears, which obviously indicates proton irradiation has a more powerful significant effect on properties of GaSb. The PL quenching by irradiation are often proposed to be radiation-induced formation of competing recombination channels or radiation produced non-radiative pathway [19,20,21]. Actually, after irradiation vancancy-type defects are introduced into materials and may act as the non-radiative recombination centers. In reference[12], S M Ka proposed the electron irradiation-induced 280 ps V_{Ga} defect was the cause of the PL quenching. It seems that there are some similarities in the proton irradiated undoped samples, however, in addition to irradiation-induced Ga monovacancies, divacancies produced by proton irradiation may also act as the non-radiative centers. This conclusion is consistent with our results that the PL intensity in undoped GaSb decreases at higher irradiation dose at which divacancies would form.

4. Conclusion

Defects in proton-irradiated undoped GaSb were studied by positron lifetime spectroscopy and photoluminescence. Monte Carlo method gave the depth distribution of vacancies induced by 2.6 MeV proton irradiation. Positron lifetime measurements indicated that vacancy-type defects were introduced after lower dose proton irradiation. After irradiation with the highest dose of 3×10^{15} cm^{-2}, divacancies were formed. In the annealing experiments two different annealing stages were observed in the as grown and proton-irradiated samples. In the as grown sample, the first between 0 and 100 ^{o}C was attributed to the annealing of V_{Ga} defects, and the second annealing stage between 300 and 500 ^{o}C was assigned to the annealing of another kind of Ga vacancies or vacancy complexes having larger mobile energy. As for the proton irradiation samples, divacancies were formed during the temperature range of 50-200 ^{o}C, resulting in a positron average lifetime peak as a function of annealing temperature. At around 500 ^{o}C all the vacancies were annealed out. By comparing the different annealing courses, it was proposed that hydrogen impurity induced by implanted proton had an active effect on the annealing process. PL results showed that the peak intensity decreased quickly after proton irradiation and it was attributed to the irradiation induced non-radiative recombination centers, the candidates of which were most likely the monovacancies or divacancies induced by proton irradiation.

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References

[1] P. S. Dutta, H.L. Bhat, V. Kumar, J.Appl.Phys. **81**, 5821 (1997).
[2] M. Hakala, M.J. Puska, R.M. Nieminen, J.Appl.Phys. **91**, 4988 (2002).
[3] C. C. Ling, M.K. Lui, S.K. Ma, X.D. Chen, S. Fung, C. D. Beling, Appl. Phys. Lett. **85**, 384 (2004).
[4] D. Shaw, Semiconductor Science and Technology **18** , 627 (2003).
[5] K. T. Short, S. J. Pearton, Journal of The Electrochemical Society **135**, 2835 (1988).
[6] J. M. Zavada, R.G. Wilson, Hydrogen implantation in III–V compound semiconductors and its redistribution with annealing., Trans Tech Publications, Switzerland, 1994.
[7] P. Hautojärvi, C. Corbel, in:A. P.Mills, Positron Spectroscopy of Solids, IOS Press, Amsterdam, 1995,p.491.
[8] R. Krause-Rehberg, H.S. Leipner, Positron Annihilation in Semiconductors, Defect Studies, Springer-Verlag, Berlin, 1999.
[9] J. F. Ziegler, J. P. Biersack, The Stopping and Range of Ions in Solids, Pergamon, New York, 1985.
[10] C. C. Ling, S. Fung, C. D. Beling, H. M. Weng, Physical Review B 64,075201 (2001).
[11] H. Xu, J. Appl. Phys. **68** , 4077 (1990).
[12] S. K. Ma, M. K. Lui, C. C. Ling, S. Fung, C. D. Beling, K. F. Li, K. W. Cheah, M. Gong, H. S. Hang, H.M. Weng, J.Phys-Conden Mat. **16**, 6205 (2004).
[13] M. Yamaguchi, Y. Itoh, K. Ando, A. Yamamoto, J. J. Appl.Phys.**25**, 1650 (1989).
[14] S. Dannefaer, W. Puff, D. Kerr, Phys. Rev. B **55**, 2182 (1997).
[15] A. Polity, T. Abgarjan, R. Krause-Rehberg, Appl. Phys.A: Mat.Sci. & Proc **60**, 541 (1995).
[16] V. Ranki, A. Pelli, K. Saarinen, Phys Rev B **69**. 115205 (2004).
[17] E. T. R. Chidley, S. K. Haywood, A. B. Henriques, N. J. Mason, R. J. Nicholas, P. J. Walker, Semiconductor Science and Technology **6**, 45 (1991).
[18] P. S. Dutta, K. S. R. Koteswara Rao, H. L. Bhat, V. Kumar, Applied Physics A: Mat Sci & Proc **61**, 149 (1995).
[19] J. Toivonen, T. Hakkarainen, M. Sopanen, H. Lipsanen, J. Oila, K. Saarinen, Appl Phys Lett **82** , 40 (2003).
[20] I. A. Buyanova, M. Wagner, W. M. Chen, B. Monemar, J.L. Lindstrom, H. Amano, I. Akasaki, Appl Phys.Lett .**73**, 2968 (1998).
[21] A. V. Gomonnai, D. B. Goyer, O. O. Goushcha, Y. M. Azhniuk, I.G. Megela, M. Kranjcee, Radiative recombination in electron-irradiated GaP crystals, Romanian Conference on Advanced Materials (ROCAM 2003), Constanta, Romania, 2003, p. 641.

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