JOURNAL OF APPLIED PHYSICS VOLUME 91, NUMBER 4 15 FEBRUARY 2002

Positron-annihilation study of compensation defects in InP

Y. Y. Shan
Department of Physics, The University of Hong Kong, People's Republic of China

A. H. Deng
Department of Applied Physics, Sichuan University, Sichuan, People's Republic of China

C. C. Ling, S. Fung, and C. D. Ling
Department of Physics, The University of Hong Kong, Hong Kong, People's Republic of China

Y. W. Zhao
Material Science Centre, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People's Republic of China

T. N. Sun and N. F. Sun
Hebei Semiconductor Research Institute, P.O. Box 179, Shijiazhuang, People's Republic of China

(Received 5 February 2001; accepted for publication 26 October 2001)

Positron-annihilation lifetime and positron-annihilation Doppler-broadening (PADB) spectroscopies have been employed to investigate the formation of vacancy-type compensation defects in *n*-type undoped liquid encapsulated Czochrolski grown InP, which undergoes conduction-type conversions under high temperature annealing. *N*-type InP becomes *p*-type semiconducting by short time annealing at 700 °C, and then turns into *n*-type again after further annealing but with a much higher resistivity. Long time annealing at 950 °C makes the material semi-insulating. Positron lifetime measurements show that the positron average lifetime τ_{av} increases from 245 ps to a higher value of 247 ps for the first *n*-type to *p*-type conversion and decreases to 240 ps for the ensuing *p*-type to *n*-type conversion. The value of τ_{av} increases slightly to 242 ps upon further annealing and attains a value of 250 ps under 90 h annealing at 950 °C. These results together with those of PADB measurements are explained by the model proposed in our previous study. The correlation between the characteristics of positron annihilation and the conversions of conduction type indicates that the formation of vacancy-type defects and the progressive variation of their concentrations during annealing are related to the electrical properties of the bulk InP material. [DOI: 10.1063/1.1428796]

I. INTRODUCTION

As an important material for the development of long wavelength optoelectronic and high frequency devices, InP has attracted a great deal of investigation in recent years. Growing interest and studies of the electrical properties of high purity InP crystal have revealed conduction-type conversions upon annealing and have led to further understanding of compensation mechanisms in this material.[1–3] Similar to GaAs, where the formation of V_{Ga} related defects upon heat treatment were found to give rise to its conduction-type conversion,[4,5] thermally induced intrinsic defects play important roles in the compensation process in InP. Thermally induced defects can, in generally, be detected by different techniques.[6,7] However, the details of the evolution and interaction processes of these defects upon different annealing duration are still poorly understood.

In this work, positron-annihilation lifetime (PAL) and positron-annihilation Doppler-broadening (PADB) spectroscopies have been employed to study the formation of defects responsible for conduction-type conversions in undoped LEC-grown *n*-type InP. Being a sensitive method for vacancylike defect probing, positron-annihilation techniques have been effectively used to characterize defects in semiconductor materials in past decades.[8,9] Studies of defect identification by positron annihilation in InP have been carried out intensively in recent years.[10–16] It has been found that positron average lifetimes of *n*-type materials are generally a few ps longer than those of *p*-type materials, indicating the presence of trapping defects.[11]

However, we found in this study that there is a small increase of τ_{av} after the *n*-type as-grown sample changes to *p*-type upon short time annealing at 700 °C. Further annealing for a longer duration reconverts the material back to *n*-type and gives rise to a shorter positron lifetime by a few ps. It is thought that some acceptor defects are thermally induced in the initial annealing process. These are probably responsible for the first type conversion and may well be the precursors of some donor defects causing the second conversion to *n*-type conduction with higher resistivity.

II. EXPERIMENT

The InP wafer used in this work was an *n*-type undoped LEC-grown single crystal, produced by the phosphorus *in situ* injection technique.[17,18] The samples were annealed in a sealed quartz tube with a 60 mbar phosphorus ambient at 700 °C for 5, 10, 20, 40, 80 h, respectively, and at 950 °C for 90 h. This phosphorus ambient prevents the InP samples from dissociation. The samples were then cooled down

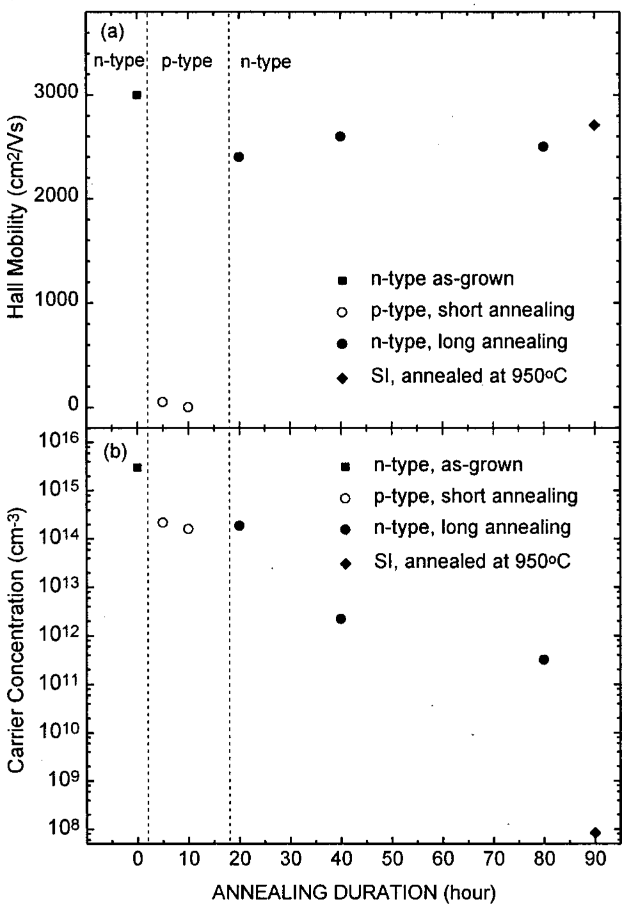

FIG. 1. Carrier concentrations and Hall mobilities of InP samples showing conduction-type conversions under different annealing duration at 700 °C. The 90 h annealing sample was annealed at 950 °C.

slowly to room temperature after annealing. Hall measurements were carried out at room temperature to characterize the electrical properties of the as-grown sample as well as those annealed ones.

Measurements by positron-annihilation lifetime (PAL) and positron-annihilation Doppler broadening (PADB) spectroscopies were carried out simultaneously. A fast-fast lifetime spectrometer with a time resolution (FWHM) of 235 ps was used to collect the PAL spectra. PADB spectra were collected by a high purity Ge detector in coincidence with a scintillator detector in order to eliminate high random background level.[19] A 3 μCi ^{22}NaCl positron source was directly deposited onto the surfaces of the samples, thus making the source annihilation and correction negligible. Each PAL and PADB spectrum contained 5×10^6 counts and was subjected to off-line software stabilization.[20]

III. RESULTS AND DISCUSSION

Figure 1 shows the carrier concentrations and Hall mobilities of the samples under different annealing durations. It is observed that the as-grown *n*-type conduction changes to *p*-type conduction after annealing for 5 and 10 h at 700 °C. The positive Hall coefficients of the two samples with short annealing durations (5 and 10 h) and their low values of mobility are indicative of the typical *p*-type conduction of bulk materials. For the longer annealing durations of 20, 40, and 80 h, the samples were converted back to *n*-type conduction again. The Hall mobility increases while its electron concentration decreases. The semi-insulating (SI) state was obtained after annealing for 90 h at higher temperature of 950 °C. A reasonable explanation for these conduction-type conversions is that acceptorlike defects are formed at the earlier stage of annealing process, followed by the dissociation of the same and formation of donor defects upon further annealing.

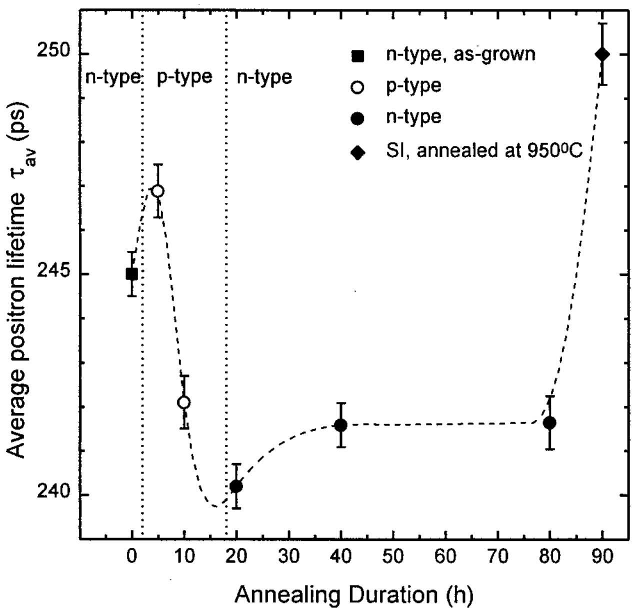

FIG. 2. Positron average lifetime as a function of annealing duration. The vertical dotted lines show approximately the boundaries of the conduction-type conversions.

The corresponding evolution of the positron average lifetime, τ_{av}, was observed and shown in Fig. 2. τ_{av} increases from 245 ps to 247 ps as the as-grown *n*-type sample became *p*-type conduction after 5 h annealing. Since the bulk positron lifetime τ_b of InP is around 236–241 ps,[13,14] the longer lifetime of 245 ps indicates the existence of some vacancy trapping defects in the as-grown *n*-type sample. A positron lifetime component of 282 ps was observed and the corresponding trapping rate and defect concentration is found to be $\sim3.3\times10^8\,\mathrm{s}^{-1}$ and $\sim1.5\times10^{16}\,\mathrm{cm}^{-3}$, respectively.[16] It has been revealed earlier that $V_{\mathrm{In}}H_4$ is the dominant shallow donor complex present in the as-grown InP and, on dissociation, positrons were found to be trapped at either V_{In} defects or hydrogen-V_{In} complexes, with a positron lifetime of 285 ps.[16,21] After a short time annealing, the $V_{\mathrm{In}}H_4$ complex dissociates into $V_{\mathrm{In}}H_n^{(n-3)}$ $(n=0,1,2,3)$ deep acceptorlike defects, turning the material into *p*-type conduction. The concentration of positron trapping sites, i.e., V_{In} and hydrogen-V_{In} complexes, increases and thus a longer τ_{av} is observed. On further annealing for a few more hours (i.e., a total of 10 h), τ_{av} decreases to 242 ps, and with the Fermi energy remaining essentially unchanged, this indicates the decrease of the V_{In} positron traps. This observation is consistent with the result of Hall measurements in Fig. 1, where

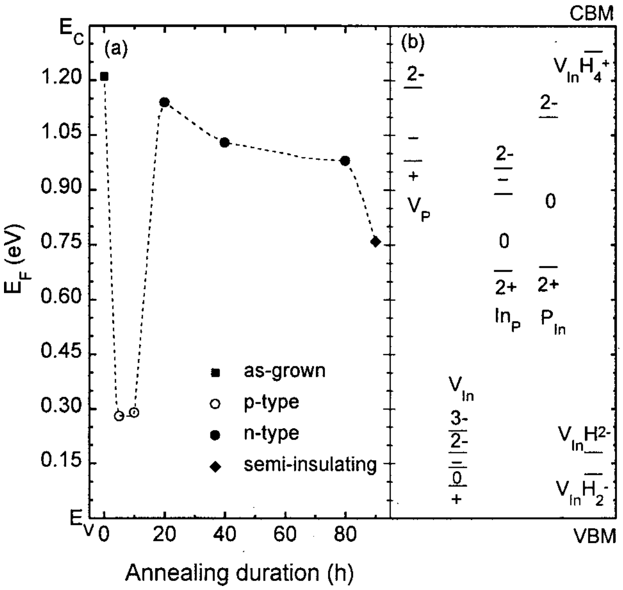

FIG. 3. (a) Values of Fermi level E_F in InP calculated from the carrier concentrations obtained from Hall measurements for samples subjected to different annealing duration at 700 °C. The 90 h annealing sample was annealed at 950 °C. The dotted line is a guide to the eye only. (b) Defect ionization levels in InP obtained from theoretical calculations (see Ref. 23 and Ref. 24).

the hole concentration decreased slightly in comparison to that of the sample with 5 h annealing.

It is well known that the relation of the Fermi level to a defect's ionization level in the band gap basically determines the defect's ionization and charge state, consequently affecting the degree of positron trapping. Figure 3 shows the Fermi levels of samples with different annealing duration, together with the ionization levels of the common defects in InP. Earlier studies show that the τ_{av} of n-type material is generally a few ps longer than that of p-type material.[11] This can naturally be explained in that E_F is close to the conduction band for n-type material, and close to valence band for p-type material. Thus there are more neutral or negatively charged donorlike defects such as V_P trapping positrons in n-type material than in p-type material. It should be noted, that τ_{av} of the as-grown n-type sample is slightly shorter than that of p-type samples converted by annealing. Although E_F moves downward after the sample turns into p-type, those deep acceptor levels of hydrogen-V_{In} complexes, produced through the dissociation upon annealing, might still be lower than the Fermi level as seen from Fig. 3. Therefore, positrons can be trapped into those defects causing a longer τ_{av} to be observed.

It has been suggested that donorlike defects form following the dissociation of the $V_{In}H_n$ acceptorlike defects formed during the annealing process. While the nature of these defects is not at present clear, the formation of P_{In}, an EL2-like antisite deep donor defect, seems probable.[21] Such defects are likely to form during annealing, since interstitial and sublattice site phosphorous atoms are likely to migrate to the V_{In} related defects, forming the P_{In} antisite defect. Thus the concentration of antisite defects increases, while that of vacancylike acceptor defect is expected to decrease. Consequently, the hole concentration and τ_{av} decreases for samples with an annealing duration of less than 20 h. Further annealing to cumulative times of more than 20 h causes the formed EL2-like donor defects to dominate and a conduction-type conversion from p-type back to n-type is observed. τ_{av} reaches its minimum value of around 240 ps, which is equivalent to its bulk lifetime value of 230–241 ps.[13,14]

After the sample changed back to n-type conductivity, a small increase of τ_{av} was observed upon further annealing. This could be explained by the formation of $V_{In}V_P$ divacancy or hydrogen associated forms of this divacancy. A study shows that the Frenkel reaction is the dominant source of native point defects in InP.[22] A large amount of V_P monovacancies form after P_P atoms migrate to interstitial sites and then to the neighboring V_{In} vacancies, forming EL2-like P_{In} antisite defects. V_P vacancies, which are in the vicinity of V_{In} vacancies, could then combine to form $V_{In}V_P$ divacancies through thermal diffusion. Positrons would then trap into those divacancies, giving rise to a longer τ_{av}. A typical positron divacancy lifetime of 330 ps, with trapping rate of $7.5 \times 10^7\,\mathrm{s}^{-1}$ and concentration of $3.0 \times 10^{15}\,\mathrm{cm}^{-3}$, was observed and was assigned to the $V_{In}V_P$ divacancy as in our recent study.[16]

Assuming the above picture the small increase of τ_{av} and its following saturation behavior after 20 h annealing also suggests that the formation of $V_{In}V_P$ divacancy was not so remarkable probably because the annealing temperature of 700 °C is not sufficient for thermally producing a high concentration of $V_{In}V_P$ divacancies. A much higher τ_{av} of 250 ps was observed for the sample annealed at 950 °C for 90 h. This is most likely not due to the formation of $V_{In}V_P$ divacancy but due to a large concentration of $V_P^{(-)}$ caused by excessive phosphorus out-diffusion.

Figure 4 shows the results of PADB measurements characterized by S and W parameters.[23,24] The general trends of S and W values throughout the conduction-type conversions under different annealing durations are in good agreement with the above interpretation of the lifetime results. The slight increase of S-value and slight decrease of W-value (to point D_1) during the first conversion from n-type to p-type indicates an increase of defect trapping. As discussed above, this is most likely to be due to a sharp increase in the negative or neutral charged V_{In}-H_n $(n=0-3)$ complexed defects that form on break-up of the $V_{In}H_4^+$ shallow donor. At this point in the annealing, trapping into V_P stops as this defect becomes positively charged when the Fermi energy lowers with no compensating $V_{In}H_4^+$. After annealing for 10–20 h brings the S parameter attains its lowest value—and from the lifetime result the point (B) obtained on the S-W plot can be identified as being very close to the bulk state. The drop in S-value probably derives from the reduction of the acceptor-like $V_{In}H_n$ defects caused by further thermal dissociation of these centers. The larger S values obtained for samples upon longer annealing duration indicate the formation of large size vacancy-type defects, such as the $V_{In}V_P$ divacancies (point D_2). Finally, throughout the longer annealings phosphorus is being lost from the sample. This is especially true at the 950 °C annealing. It is thus expected that V_P will begin to play a dominant role especially as the Fermi-energy is now

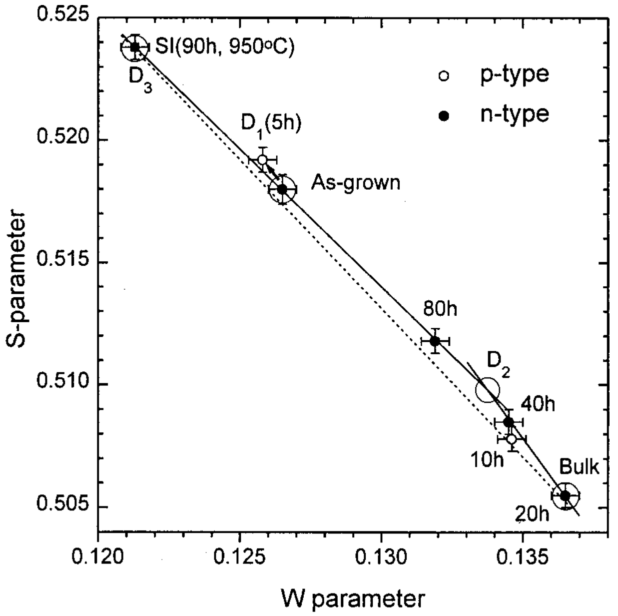

FIG. 4. The S-W plot of PADB data taken on InP under different annealing durations. Points D_1, D_2, and D_3 are attributed to significant annihilation fractions in $V_{\mathrm{In}}H_n$, $V_{\mathrm{In}}V_{\mathrm{P}}$, and V_{P}, respectively. The dotted line is drawn between the bulk state and the estimated V_{P} state and indicates that the primary defect in the as-grown and semi-insulating (SI) states is V_{P}.

in the upper half of the band gap. Point D_3 is thus attributed to a significant fraction of V_{P} trapping, which is consistent with the fact that the as-grown sample lies on the D_3-B line, indicating a predominance of V_{P} trapping in the as-grown state.

The tentative nature of the interpretation of the PAL and PADB data requires that further studies be made. Such studies should include temperature dependent PAL, coincidence Doppler-broadening, and the measurement of temperature dependence of positron effective diffusion length by mean of slow positron beam. Such measurements are planned in order to characterize the defects in annealed InP more specifically; for example, by considering their concentration variation, trapping rates, and charge states.

IV. CONCLUSIONS

In summary, the formation of various vacancy type defects in undoped LEC InP upon annealing for different duration at 700 °C were detected by positron-annihilation techniques. These defects, which can compensate each other, are responsible for the conduction-type conversions from as-grown *n*-type to *p*-type, and then back to *n*-type with a higher resistivity. An increase of positron average lifetime τ_{av} was observed after the first conversion from *n*-type to *p*-type, where the as-grown shallow donor $V_{\mathrm{In}}H_4$ complex dissociated into acceptorlike defects, characterized by a positron lifetime of 285 ps. The formation of the antisite donor defect P_{In} causes the decrease of the concentration of vacancy acceptors, consequently giving rise to the decrease of τ_{av}. $V_{\mathrm{In}}V_{\mathrm{P}}$ divacancies can effectively form upon long time annealing at high temperatures, along with a possible conversion to the semi-insulating state. The formation of these intrinsic defects is critical for the electrical properties of undoped LEC InP.

ACKNOWLEDGMENTS

The work described in this paper was partially supported by the grants from the Research Grant Council of the Hong Kong Special Administrative Region, China (under Project No. HKU7137/99P). Valuable discussions with Dr. X. D. Chen are acknowledged.

[1] D. Hofmann, G. Müller, and N. Streckfuss, Appl. Phys. A: Solids Surf. **48**, 315 (1989).
[2] G. Hirt, D. Hofmann, F. Mosel, N. Schafer, and G. Müller, J. Electron. Mater. **20**, 1065 (1991).
[3] R. Fornari, A. Brinciotti, E. Gombia, R. Mosca, and A. Sentiri, Mater. Sci. Eng., B **28**, 95 (1994).
[4] D. C. Look and G. S. Pomrenke, J. Appl. Phys. **54**, 3249 (1983).
[5] N. H. Ky and F. K. Reinhart, J. Appl. Phys. **83**, 718 (1998).
[6] G. Hirt, D. Wolf, and G. Müller, J. Appl. Phys. **74**, 5538 (1993).
[7] P. Kipfer, J. Lindolf, D. Hofmann, and G. Müller, J. Appl. Phys. **69**, 3860 (1991).
[8] See for review P. Hautojärvi and C. Corbel in *Positron Spectroscopy of Solids*, Proceedings of the International School of Physics, edited by "Enrico Fermi" A. Dupasquier, A. P. Mills, Course **CXXV**, (North-Holland, Amsterdam, 1994).
[9] R. Krause-Rehberg and H. S. Leipner, *Positron Annihilation in Semiconductors: Defect Studies*, Spinger Series in Solid-state Sciences, **127** (Springer-Verlag, Berlin, 1999).
[10] T. Bretagnon, S. Dannefaer, and D. Kerr, J. Appl. Phys. **73**, 4697 (1993).
[11] Z. Q. Chen, X. W. Hu, and S. J. Wang, Appl. Phys. A: Mater. Sci. Process. **66**, 435 (1998).
[12] A. Polity and T. Engelbrecht, Phys. Rev. B **55**, 10480 (1997).
[13] G. Dlubek and R. Krause, Phys. Status Solidi A **102**, 443 (1987).
[14] A. P. Seitsonen, R. Virkkunen, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **49**, 5253 (1994).
[15] M. Törnqvist, C. Corbel, L. Liszkay, K. Saarinen, P. Hautojärvi, Mater. Sci. Eng., B **28**, 125 (1994).
[16] C. D. Beling, A. H. Deng, Y. Y. Shan, Y. W. Zhao, S. Fung, N. F. Sun, T. N. Sun, and X. D. Chen, Phys. Rev. B **58**, 13 648 (1998).
[17] J. Fargers, *et al.*, J. Cryst. Growth **59**, 665 (1982).
[18] D. F. Bliss, *et al.*, J. Electron. Mater. **20**, 967 (1991).
[19] M. Alatalo, H. Kauppinen, K. Saarinen, M. J. Puska, J. Mäkinen, P. Hautojärvi, and R. M. Nieminen, Phys. Rev. B **51**, 4176 (1995).
[20] A. P. Huang, C. C. Ling, S. Fung, C. D. Beling, C. W. H. Lam, and C. Y. Chung, Mater. Sci. Forum **255–257**, 454 (1997).
[21] Y. W. Zhao, X. L. Xu, M. Gong, S. Fung, C. D. Beling, X. D. Chen, N. F. Sun, T. N. Sun, S. L. Liu, G. Y. Yang, X. B. Guo, Y. Z. Sun, L. Wang, Q. Y. Zheng, Z. H. Zhou, and J. Chen, Appl. Phys. Lett. **72**, 2126 (1998).
[22] D. T. J. Hurle, J. Appl. Phys. **85**, 6957 (1999).
[23] A. P. Seitsonen, R. Virkkunen, M. M. Puska, and R. M. Nieminen, Phys. Rev. B **49**, 5253 (1994).
[24] C. P. Ewels, S. Orberg, R. Jones, B. Pajot, and P. R. Briddon, Semicond. Sci. Technol. **11**, 502 (1996).