Formation of V_P-Zn complexes in bulk InP(Zn) by migration of P vacancies from the (110) surface

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We apply a combination of positron annihilation spectroscopy and scanning tunneling microscopy to show that thermally generated P vacancies diffuse from the InP surface toward the bulk. The defect observed in the bulk can be identified as a complex consisting of a P vacancy and a Zn impurity. We infer that this pair is formed when the diffusing positive P vacancy is trapped at the Zn dopant. A rough estimate for the migration energy of the P vacancy results in a value of 1.3 eV.

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In recent years, scanning tunneling microscopy (STM) has successfully been utilized in the study of semiconductor surfaces. By cleaving the samples in ultrahigh vacuum (UHV) it has become possible to reproducibly prepare clean surfaces and thus to study defect formation and interaction of defects on the surface, as well as the influence of defects on the electronic properties of the semiconductor. Clean InP 110 surfaces has been the focus of several studies. The charge state dependence on the relaxation around P vacancies on InP(110) and GaP(110) surfaces was studied by Ebert *et al.*,[1] furthermore the formation of P vacancies at low temperatures by Langmuir evaporation[2] and the interaction of vacancies on InP(110) surfaces was investigated by the same group.[3] In a study on Zn doped InP(110) surfaces Ebert *et al.* came to the conclusion that subsurface defect complexes are formed when the samples are annealed at 480 K. It was concluded that the defect complex consisted of a subsurface P vacancy and a Zn atom. More recently the influence of the Fermi-level effect on surface vacancy formation has been studied both experimentally and theoretically.[4–6]

This V_P-Zn complex has been the focus of several positron annihilation spectroscopy (PAS) studies in bulk InP. Dlubek *et al.*[7] detected Zn dopant related vacancy type defects in InP and found that the defect is annealed out above 700 K. The defect was later identified by Alatalo *et al.*,[8] who compared core electron annihilation spectroscopy results with theoretical calculations, and verified that the defect was the P vacancy Zn dopant pair. Mahony *et al.*[9] studied the contribution of the P vacancy Zn dopant pair to the saturation of the carrier concentration.

Recently Slotte *et al.* studied the thermal formation of the V_P-Zn in the temperature interval 500–650 K.[10] In this work it was shown that the complex is formed when a migrating P vacancy encounters a Zn dopant and pairs with it. The origin of the P vacancy could not be determined, since the positive charge of the unpaired P vacancy makes it invisible in the PAS experiment. However, a significant contribution of P vacancies generated at the surface in the formation of the V_P-Zn complex could be ruled out. A Zn concentration above 5×10^{18} cm^{-3} at an annealing temperature 540 K, or an approximately 100 K higher annealing temperature with a lower Zn concentration, was required in these experiments to produce an observable concentration of V_P-Zn. It can also be noted that the surface orientation in this study was (100).

In the present work, we combine the surface investigation tool STM with the subsurface investigation tool PAS, thus confirming the subsurface formation of Zn related vacancy complexes when clean InP(110) surfaces are annealed. Positron annihilation spectroscopy enables the direct identification and quantification of vacancy defects.[11,12] Thermalized positrons get trapped at vacancies where the positive charge of the ion cores is missing. At vacancies the electron density is reduced compared with that of the perfect lattice. Hence, the positron lifetime increases and the momentum distribution of the annihilating e^+-e^- pair narrows. The latter can be observed as Doppler broadening of the 511 keV e^+-e^- annihilation radiation.

In our experiment we use Czochralski (LEC)-grown single InP crystals. The samples were *p* type, doped with Zn to a concentration of 2×10^{18} cm^{-3}, which is significantly lower than the required Zn concentration for bulk formation of V_P-Zn.[10] In order to reproducibly prepare clean surfaces with a low defect concentration the samples were cleaved along the (110) plane in ultrahigh vacuum (pressure 5×10^{-9} Pa). After cleavage the samples were annealed in the temperatures 525 K and 540 K for 24–400 h. After annealing the samples were kept in air. The sample surfaces were monitored with a scanning tunneling microscope (STM) during the annealing process, without breaking the vacuum.

Positron annihilation spectroscopy measurements were done using a slow positron beam in order to study vacancy type defects beneath the sample surface. In the Doppler broadening experiment the different shapes of the annihilation line (momentum distribution) is usually described by the momentum parameters *S* and *W*. *S* is the low momentum parameter and describes annihilation mainly with valence electrons and *W* is the high momentum parameter, which describes annihilation mainly with core electrons. An increase in the *S* parameter is a clear sign that vacancy type defects are detected. The Doppler broadening measurements were performed at room temperature as a function of the positron implantation energy. To detect the annihilation ra-

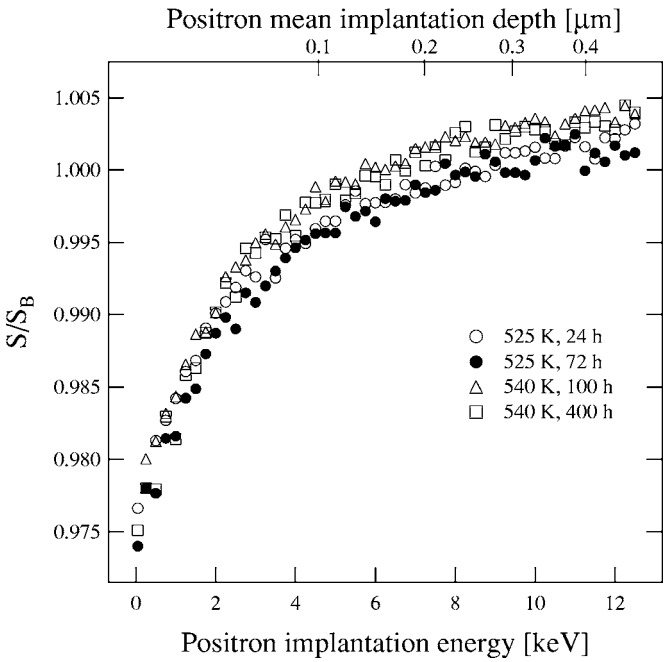

FIG. 1. *S* parameter as a function of positron implantation energy for samples annealed at 525 K and 540 K. The mean positron implantation depth is also indicated in the figure.

diation we use a Ge detector with an energy resolution of 1.3 keV at 500 keV. The *S* and *W* parameter windows were chosen to $(0-3.4)\times10^{-3}$ m_0c and $(11-27)\times10^{-3}$ m_0c, respectively.

In previous studies[13] it has been observed that the concentration of observed Zn atoms on the surface at annealing temperatures above 480 K is decreasing as a function of annealing time. Two possible explanations for this are discussed in Ref. 13, (i) the formation of Zn related charge compensating defects in the subsurface layers that make the Zn atoms on the surface invisible and (ii) the real depletion of the Zn concentration in the surface by Zn diffusion. The second explanation can be ruled out since much higher temperatures are required for this process.[14,15] The formation of Zn related defect complexes is most likely linked with the fact that the thermal formation rate of P vacancies on InP 110 surfaces decreases above 435 K.[2] This decrease was explained by out diffusion of phosphorus from the bulk. This out diffusion process could lead to either P_i-Zn or V_P-Zn subsurface complexes. In Ref. 13 it is stated that the latter complex is the most likely candidate. The reason for this is that to make a Zn atom invisible in the STM experiment it has to be compensated by defect that has a $+1e$ charge and it is predicted that the P interstitial has a $+3e$ charge in *p* type InP, whereas the P vacancy has a $+1e$ charge.

Figure 1 shows the *S* parameter as a function of positron implantation energy. The *S* parameter is normalized to the InP(110) bulk value. The mean implantation depth of the positrons is also indicated in the figure. The decrease in the *S* parameter toward lower implantation energy is due to the fact that a significant fraction of the positrons is diffusing to the surface where the characteristic *S* parameter is low. This also causes a corresponding raise in the *W* parameter. It can

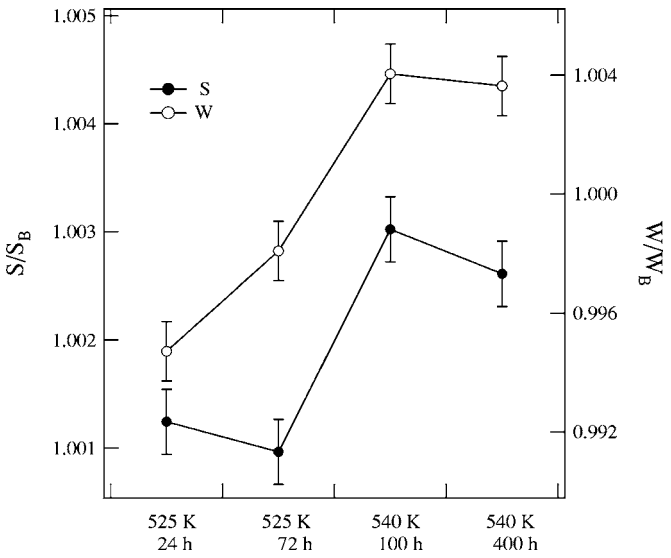

FIG. 2. The average of the *S* and *W* parameters in the positron implantation energy interval 9–11 keV for the different samples.

be noted that the values for the surface *S* and *W* parameters are approximately equal for all the samples.

At energies above approximately 8 keV the *S* parameter level out at values characteristic for the samples. For samples annealed at 525 K only a very small increase in the *S* parameter at high energies can be detected. For all samples annealed at 540 K, the *S* parameter values deeper in the samples are clearly higher than the bulk value. This indicates that vacancy type defects have been formed. Due to the large scatter in the *W* parameter values, which is due to less counts in the wing region of the spectrum, we show in Fig. 2 the average of the *S* and *W* parameters for the energy interval 9–11 keV for all the samples. From the *W* parameter plot we can note that also the *W* parameter in these samples is higher than the bulk value.

The measured *S* and *W* parameters are superpositions of the different annihilation states in the sample, e.g., for a sample with only one type of defect the *S* and *W* values will be

$$S = (1 - \eta_D)S_B + \eta_D S_D, \tag{1}$$

$$W = (1 - \eta_D)W_B + \eta_D W_D, \tag{2}$$

where η_D is the fraction of positron annihilating in the defect state *D*. The equations above will form a segment of straight line between the defect state (S_D, W_D) and the bulk state S_B, W_B in the *S*-*W* plane. In the $S(W)$ plot shown in Fig. 3, the measured *S* and *W* values for these samples lie almost completely on a line between the surface state and the bulk state. The samples annealed at 540 K are clearly off the line connecting the bulk and surface state. This is due to the fact that the *S* and *W* parameters for these samples will be superpositions of three annihilation states, the surface, the bulk and the vacancy state. The vacancy has a larger characteristic *S* parameter value than the bulk lattice, but interestingly its *W* parameter is close to or even larger than W_B.

The high values of the *W* parameters indicate that the

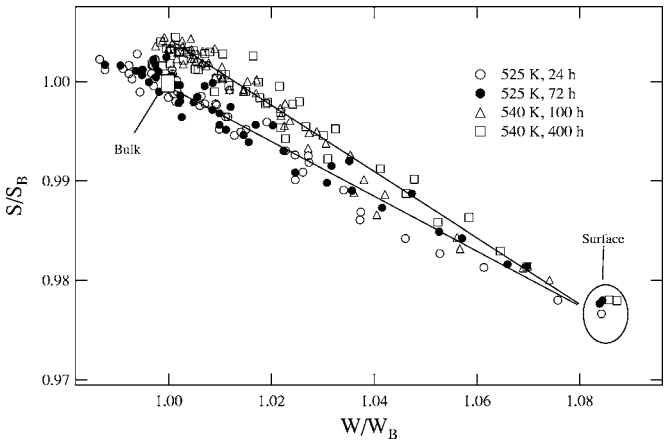

FIG. 3. $S(W)$ plot of the samples annealed at 525 K and 540 K. For the samples annealed at 540 K, the S and W values are superposition of the bulk, defect and surface states, where as for the samples annealed at 525 K the values are only superposition of the bulk and surface states. The bulk and surface states are indicated in the figure. The lines are guides to the eye.

thermally generated vacancy is surrounded by atoms with a large numbers of core electrons. The same effect has been observed for P vacancies formed in electron irradiations and it can be attributed to the $4d$ electrons of the In atom and the $3d$ electrons of the Zn atom.[8] The vacancy type defect is thus related to the P sublattice. The P vacancy is in a positive charge state $(+1e)$ in p type InP (Refs. 16 and 17) and therefore an isolated P vacancy cannot be detected by positrons in these samples. However, the V_P-Zn pair can be expected to be in neutral charge state since it consists of a positively charge P vacancy and a negatively charged Zn dopant. We can thus identify the detected vacancy-type defect as a P vacancy Zn dopant pair, V_P-Zn. We infer that this pair is formed when a P vacancy migrates from the surface into the bulk and pairs with the Zn dopant. Formation of the complex directly in the bulk or by P vacancy formation in the bulk and pairing with the Zn dopant can be ruled out, since the Zn concentration and the annealing temperatures are too low for bulk formation of the complex.[7,10]

The STM measurements show that P vacancies are formed on the (110) surface. A reduction in the observable Zn concentration is also seen in the experiments.[13] This apparent Zn depletion is suggested to be due to the formation of neutral subsurface defect complexes, most likely a complex consisting of the P vacancy and the Zn dopant. The PAS experiments now prove that this conclusion is correct. This process is observed in the STM measurements at annealing temperatures around 470 K, whereas a 70 K higher annealing temperature is required to make the process observable in the PAS experiments. The explanation for this could be that the 525 K is not a high enough temperature to migrate P vacancies in InP or the annealing times are too short, which prevents the formation of an observable concentration of V_P-Zn complexes. The surface concentration of P vacancies could also be too low at 525 K to yield a diffusion tail with a high enough defect concentration to be detected in the positron annihilation experiments.

A estimate for the minimum value of the diffusion coefficient for the P vacancy in InP can be done from Fig. 1 and the mean positron implantation depth. From the definition of the diffusion length

$$L = \sqrt{4Dt}, \tag{3}$$

we get a value of $D=0.2$ nm^2/s at 540 K. Furthermore, by assuming a jump frequency at infinite temperature close to the measured Debye frequency[18] in InP we get a rough estimate for the migration energy by using the following relation:

$$D = \frac{1}{12}\lambda^2 \nu_0 \exp\left(\frac{S}{k}\right)\exp\left(-\frac{E_M}{kT}\right), \tag{4}$$

where λ is the lattice constant and ν_0 the Debye frequency. This yields a value of 1.3 eV for the migration energy. Within experimental errors, this estimate is consistent with our earlier study of P vacancy migration in bulk InP,[10] which yielded an migration energy for the P vacancy of 1.8 ± 0.2 eV.

In conclusion, we have used positron annihilation spectroscopy to confirm the formation of subsurface V_P-Zn complexes in Zn doped InP suggested by previous STM surface studies of clean (110) InP surfaces. The complex forms when a positively charged P vacancy, which is formed on the (110) surface, migrates into the bulk and pairs with a negative Zn dopant. An estimate of 1.3 eV for the migration energy of the P vacancy is obtained from the experimental results.

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[1] P. Ebert, K. Urban, and M. G. Lagally, Phys. Rev. Lett. **72**, 840 (1994).
[2] P. Ebert, M. Heinrich, M. Simon, K. Urban, and M. G. Lagally, Phys. Rev. B **51**, 9696 (1995).
[3] P. Ebert, X. Chen, M. Heinrich, M. Simon, K. Urban, and M. G. Lagally, Phys. Rev. Lett. **76**, 2089 (1996).
[4] U. Semmler, M. Simon, P. Ebert, and K. Urban, J. Chem. Phys. **114**, 445 (2001).
[5] U. Semmler, P. Ebert, and K. Urban, Appl. Phys. Lett. **77**, 61 (2000).
[6] K. Tanimura, Phys. Rev. B **69**, 033301 (2004).
[7] G. Dlubek, O. Brümmer, F. Plazaola, P. Hautojärvi, and K. Naukkarinen, Appl. Phys. Lett. **46**, 1136 (1985).
[8] M. Alatalo, H. Kauppinen, K. Saarinen, M. J. Puska, J. Mäkinen, P. Hautojärvi, and R. M. Nieminen, Phys. Rev. B **51**, 4176 (1995).
[9] J. Mahony and P. Mascher, J. Appl. Phys. **80**, 2712 (1996).
[10] J. Slotte, K. Saarinen, A. Salmi, S. Simula, R. Aavikko, and P. Hautojärvi, Phys. Rev. B **67**, 115209 (2003).

[11] K. Saarinen, P. Hautojärvi, and C. Corbel, *Identification of Defects in Semiconductors*, edited by M. Stavola (Academic Press, New York, 1998).
[12] R. Krause-Rehberg and H. S. Leipner, *Positron Annihilation in Semiconductors* (Springer, Berlin, 1999).
[13] P. Ebert, M. Heinrich, M. Simon, C. Domke, K. Urban, C. K. Shih, M. B. Webb, and M. G. Lagally, Phys. Rev. B **53**, 4580 (1996).
[14] S. Yu, T. Y. Tan, and U. Gösele, J. Appl. Phys. **69**, 3547 (1991).
[15] T. Litong, Z. Junglong, and F. Dunfu, Mater. Sci. Forum **61**, 29 (1990).
[16] M. Alatalo, R. M. Nieminen, M. J. Puska, A. P. Seitsonen, and R. Virkkunen, Phys. Rev. B **47**, 6381 (1993).
[17] H. Xu, Phys. Rev. B **42**, 11295 (1990).
[18] R. Trommer, H. Müller, M. Cardona, and P. Vogl, Phys. Rev. B **21**, 4869 (1980).