Divacancy defects in germanium studied using deep-level transient spectroscopy

M. Christian Petersen and A. Nylandsted Larsen*
Department of Physics and Astronomy and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, DK-8000 Aarhus C, Denmark

A. Mesli
IM2NP (UMR 6242), Faculté des Sciences et Techniques, CNRS, Campus de Saint-Jérôme, F-13397 Marseille Cedex, France
(Received 14 April 2010; revised manuscript received 17 July 2010; published 6 August 2010)

The divacancy defect in germanium is surrounded with substantial controversy. In this work past speculations about the presence and nature of this defect are critically reviewed. A detailed deep-level transient spectroscopy (DLTS) investigation of radiation damage introduced in *p*-type germanium diodes by high-energy electrons, protons, and alpha particles has been carried out. As a result it is concluded that the divacancy defect introduces only a single energy level at $E_v+0.19$ eV in the band gap as seen by DLTS. The annealing temperature of the corresponding DLTS peak is found to be 415 K. It is further argued that the observed transition involves two holes due to the presence of a single acceptor and a double acceptor with an Anderson negative-*U* ordering. We observe that the divacancy is not present after low-temperature electron irradiation. This is ascribed to vacancy capture, transforming the divacancy into a trivacancy.

DOI: 10.1103/PhysRevB.82.075203 PACS number(s): 71.55.Ak

I. INTRODUCTION

The divacancy is an important and well-characterized defect in silicon.[1,2] It is the dominant electrically active radiation-induced defect in carbon and oxygen lean silicon of resistivity higher than about 1 Ω cm. In the case of germanium one would thus intuitively expect the divacancy to play a role as well. Unfortunately one of the key techniques used for defect studies in silicon, electron paramagnetic resonance (EPR), has not been widely successful for germanium due to the many naturally occurring isotopes and high nuclear spin of germanium (particularly ^{73}Ge). As a consequence the findings reported in the literature regarding the divacancy in germanium are not as clear as for silicon.

In the following a review of the literature relating to divacancies in germanium is given. To elaborate on the topic a detailed deep-level transient spectroscopy (DLTS) investigation of the energy levels introduced in *p*-type germanium by irradiation with electrons, protons, and alpha particles at energies of several mega electron volts has been carried out, and the results are compared to literature data.

II. REVIEW OF LITERATURE

During the past two decades several studies have employed $Si_{1-x}Ge_x$ alloys to be able to follow the energy levels of radiation-induced defects as the composition moves gradually from pure silicon toward pure germanium.[3,4] The general trend is that the energy levels move closer to the valence band as the germanium content is increased. While none of the mentioned studies appear to have succeeded in using alloys with more than 50% germanium, extrapolation of the observed energy-level shifts for the only two defects for which it has been possible to compare results from such an extrapolation with observations, namely, the antimony-vacancy[3] and oxygen-vacancy[5] centers agree well with the energy levels found in pure germanium. This might seem surprising as these extrapolations include both shallow and deep levels, and, for at least the deep levels, the local structure of the defect plays an important role in determining the electrical levels. The fact that the extrapolation works well indicates that vacancy-type defects stabilize preferably with Ge-rich surroundings. Thus this extrapolation could be considered a good empirical method for predicting approximate energy-level positions in germanium. In the case of the divacancy, the two acceptor levels and the donor level have been followed in $Si_{1-x}Ge_x$ alloys up to a content of 50% germanium.[6] The basic result is that the single donor level moves down into the valence band or becomes too shallow to detect, the single acceptor level crosses midgap becoming a hole trap and the double acceptor appears to be crossing midgap slightly above the 50% germanium mark. Barring the possibility of a triple acceptor level emerging from the conduction band, we would therefore expect the divacancy to be active only in the bottom half of the band gap. Making a crude extrapolation of the above results while taking into account the detailed variation in the band edges with germanium content,[7] the position of the single acceptor is approximated to be $E_v+0.12$ eV and the double-acceptor position to be $E_v+0.19$ eV. Additionally it should be mentioned that av Skardi *et al.*[6] saw no apparent trend of a changing annealing temperature of the divacancy with germanium content.

More recently a density-functional theory study has been carried out on the divacancy in germanium,[8] predicting the defect to be stable and to possess energy levels in the band gap. The resulting energy levels correspond to the charge states also found for the divacancy in silicon; from doubly negative to singly positive. For the donor level the position is calculated to be $E_v+0.03$ eV, which is thus very shallow and in agreement with the level possibly being degenerate with the valence band as remarked above. Both acceptor levels are predicted to be located slightly below midgap with the single acceptor at $E_v+0.3$ eV. Meanwhile the position of the double acceptor relative to the valence band depends on the value used for the band-gap energy. This places the energy

level between $E_v+0.26$ eV and $E_v+0.33$ eV, thus indicating a possible negative-U ordering of the acceptor levels.[9] These theoretical values agree with the extrapolation introduced above in the sense that both methods indicate that a single- and a double-acceptor level of the divacancy should be present in the lower part of the band gap.

Early infrared absorption measurements were interpreted as showing the presence of divacancies in irradiated germanium.[10] However this attribution was later questioned[11] and there is at present no firm optical evidence of the presence of divacancies in germanium. Likewise, only a few EPR studies have been carried out on germanium[12,13] and neither assigned any observations to the divacancy.

Several DLTS studies on n-type germanium diodes have more or less tentatively assigned some DLTS peaks to the divacancy. Electron irradiation of commercial high-resistivity diodes led to the conclusion that two energy levels (labeled E4 and E5) are related to the divacancy.[14] This conclusion was based on the energy threshold for defect introduction apparently being higher for these energy levels. Another study comparing neutron and gamma irradiations of germanium diodes[15] assigned one energy level only appearing in neutron irradiations to the divacancy by comparison with the results of Poulin and Bourgoin.[14] Comparison of electron and proton irradiations of n-type germanium diodes revealed a shoulder to the E center (labeled $E_{0.29}$) only present after proton irradiation which was argued to possibly correspond to an energy level of the divacancy.[16] We have subsequently carried out further studies using alpha-particle irradiations to elaborate on this shoulder which showed that the underlying defect is not a primary defect.[17] From the observations in silicon,[18] we consider it unlikely that the divacancy would not form as a primary defect, thus ruling out the shoulder as an energy level of this defect. The energy levels observed by Poulin and Bourgoin[14] labeled E4 and E5 bear some resemblance with $E_{0.30}$ and $E_{0.23}$ found by Fage-Pedersen *et al.*[16] However the latter study saw no indication that these peaks should be related to the divacancy. Furthermore the high-irradiation doses used by Poulin and Bourgoin[14] ($0.1-2\times10^{16}$ cm^{-2}) coupled with the unknown impurity content in the diodes and a general difficulty of determining the displacement threshold makes their results questionable. In addition the presence of two majority carrier energy levels of the divacancy in n-type germanium is not consistent with the observation by av Skardi *et al.*[6] that at least the single acceptor becomes a hole trap in $Si_{1-x}Ge_x$ as x is increased.

Recently a positron annihilation spectroscopy study by Kuitunen *et al.*[19] on n-type germanium exposed to neutron irradiation has revealed important evidence of the presence of divacancies in germanium. Immediately after irradiation a component of the positron lifetime consistent with an open volume defect of divacancy size was observed. It is generally observed that germanium crystals become more p type as a result of irradiation.[11] The recovery, as a consequence of annealing at 473 K, from this conversion was seen by Kuitunen *et al.*[19] to result in the divacancies changing from being neutral to being negatively charged. These results therefore support the indications discussed above given by theory and experiments on $Si_{1-x}Ge_x$ that the divacancy in germanium is stable at room temperature and possess one or more acceptor levels.

We have earlier claimed that the divacancy cannot be related to any stable traps at room temperature observed in p-type Ge by DLTS.[20] This conclusion was based on 2 MeV proton and alpha-particle irradiations with the diodes kept at 22 K and where the subsequent DLTS measurements were done only after a heating up to room temperature. As will become apparent from the discussion of the present results, under these conditions the divacancies, which might form as a result of the low-temperature irradiations, will convert to larger vacancy complexes, probably trivacancies, when the monovacancies become mobile at a temperature of 200 K.[21]

III. EXPERIMENTAL DETAILS

Samples for this study were prepared from p-type gallium-doped, carbon and oxygen lean Czochralski-grown germanium substrates from UMICORE. Two different types of substrates were used; one for low-resistivity (LR) samples with a doping level of 1.8×10^{15} cm^{-3} and one for high-resistivity (HR) samples with a doping level of 4.4×10^{14} cm^{-3}. Diodes were made by a mesa etch following the growth of an antimony-doped n^+ top layer by molecular-beam epitaxy. This process for making n^+p germanium mesa diodes is described in greater detail in Ref. 22. The resulting diodes have an area of ~0.4 mm^2 and are mounted on TO5 headers using silver paste. The back side Ohmic contact is made by scratching an eutectic InGa alloy on the substrate while the front side contact is formed by ultrasonic bonding of a thin aluminum wire. The samples are irradiated with electrons, protons, or alpha particles at a typical energy of 2 MeV with varying doses using a Van de Graaff accelerator. The electronic levels due to the defects introduced by irradiation are characterized using DLTS and Laplace DLTS. Prior to irradiation the samples were checked by measuring the capacitance-voltage characteristics and by doing a DLTS scan to ensure no traps are present at detectable concentrations. The irradiation setup allows cooling of the sample down to 20 K as well as DLTS measurements online, making low-temperature irradiations and *in situ* DLTS measurements possible.

IV. RESULTS AND DISCUSSION

Figure 1 shows a DLTS spectrum resulting from irradiation of an n^+p-germanium mesa diode with 2 MeV electrons at room temperature (RT, $\sim$300 K). The DLTS pulse settings were chosen such as to exclude the two energy levels of the antimony-vacancy pair.[22] One of the three lines present in the spectrum can be identified as the single acceptor level of the vacancy-oxygen pair[23] (A center) by comparison with minority carrier transient spectroscopy experiments on n-type Ge.[24] The remaining two lines H140 and H190, which are labeled according to their apparent enthalpy of ionization, are thus the only candidates for energy levels of the divacancy in germanium. H140 has an apparent enthalpy of ionization of $E_{pa}(H140)=0.138$ eV and an apparent capture cross section of $\sigma_{pa}(H140)=1.2\times10^{-14}$ cm^2. For H190 the

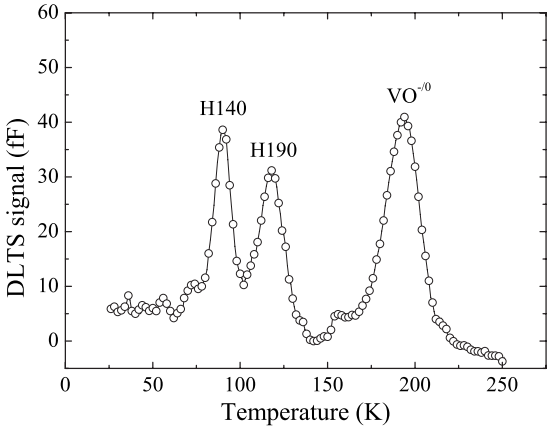

FIG. 1. A DLTS spectrum after 2 MeV electron irradiation of a LR n^+p germanium diode at RT to a dose of 2.3×10^{15} cm^{-2}. The spectrum was measured at a rate window of 868 s^{-1} with a filling pulse from −10 to −5 V and a pulse duration of 80 μs.

parameters are $E_{pa}(H190)=0.186$ eV and $\sigma_{pa}(H190)=5\times10^{-15}$ cm^2. By irradiating diodes, made from material with the two different doping levels available, with the same electron dose, it was determined that the concentration of H140 and H190 is not affected by the gallium concentration. Thus it is concluded that none of these defects involve gallium in their structure. While the emission rate of H190 does not exhibit a measurable field dependence, the emission rate of H140 shows a field dependence consistent with a phonon-assisted tunneling mechanism[25] as demonstrated in Fig. 2.

In addition, the capture cross section of H140, measured directly by varying the filling pulse duration, has a weak temperature dependence with $\sigma_p(H140)=4.2\times10^{-15}\times\exp(-0.0029\ \text{eV}/k_BT)$ cm^2. It can be speculated that H140 is a donor level due to the lack of a Poole-Frenkel effect on the field dependence of the emission rate for low electric fields, which if present would indicate an acceptor character. Further the moderate magnitude of the capture cross section could also fit a single donor level. As discussed above, the

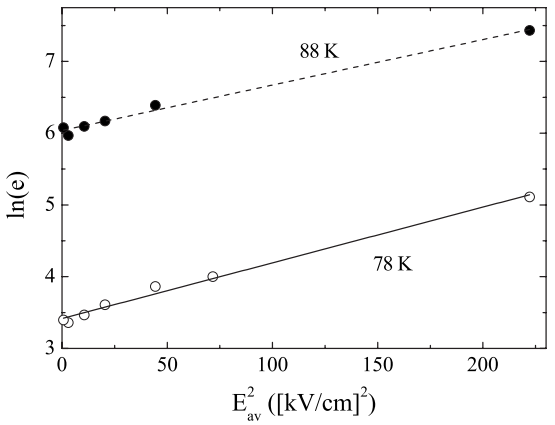

FIG. 2. The dependence of the emission rate of H140 on the average electric field in the space-charge region at two different temperatures. The straight lines are linear fits demonstrating the agreement with a phonon-assisted tunneling mechanism ($\ln[e(\mathcal{E})/e(0)]\propto\mathcal{E}^2$).

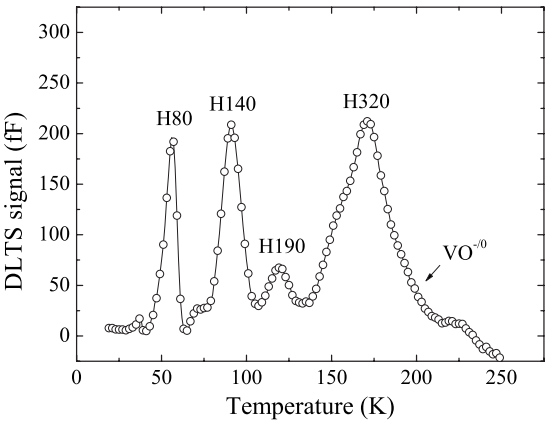

FIG. 3. A DLTS spectrum recorded after 2 MeV proton irradiation of a LR n^+p germanium diode at RT to a dose of 2.2×10^{13} cm^{-2}. The spectrum was recorded at a rate window of 868 s^{-1} with a filling pulse from −10 to −5 V and a pulse duration of 80 μs.

observation of a deep donor level of the divacancy in germanium is not expected from theory and $Si_{1-x}Ge_x$ experiments.

Even if this expectation is unwarranted, one would then surely expect the acceptor levels to be present deeper in the band gap. While H140 and H190 are, in fact, found to have very nearly the same annealing temperature (around 415 K) and similar amplitudes in RT electron-irradiated samples, it will be shown later that they are not correlated. Therefore if H140 is indeed a donor level it is not an energy level of the divacancy. In the case of H190, the actual capture cross section could not be determined since a reduction in the filling pulse duration to as little as 50 ns did not affect the amplitude of the H190 peak substantially. Hence the capture cross section is very high, on the order of 10^{-13} cm^2 or higher. Despite the absence of a field effect this strongly favors an acceptor character of H190. To investigate the H140 and H190 energy levels further we switched from electron irradiation to proton irradiation, as this strongly increases the energy transfer to the lattice atoms involved in the displacement (by up to about a factor of 500). This increased energy transfer is expected to enhance the production of higher order vacancy defects such as the divacancy. Figure 3 shows the result of a RT 2 MeV proton irradiation of an n^+p-germanium mesa diode. It is evident that at least two new dominant features, labeled H80 and H320, have emerged (the shoulder present on the low-temperature side of the H320 peak could not be resolved by Laplace DLTS), and that the H190 and the VO lines are still of about equal intensities but smaller than the two new lines; the H140 line has grown in intensity relative to the H190 line. The two new peaks have previously been reported and were found to be present in alpha-particle irradiations as well,[26] demonstrating that they are not related to the irradiation species. More specifically these defects are thus not hydrogen related. It is therefore clear that we are dealing with one or more defects that are too complicated to be produced at a measurable concentration by irradiation with 2 MeV electrons.

It is possible that the formation of these defects require displacement of several neighboring lattice atoms which is

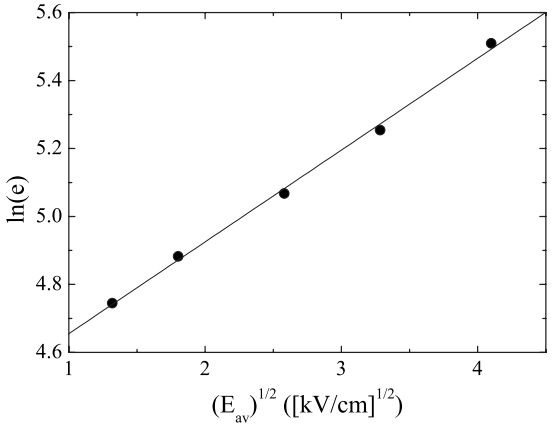

FIG. 4. The dependence of the emission rate of H80 on the average electric field in the space-charge region at 40 K indicating a Poole-Frenkel mechanism ($\ln[e(\mathcal{E})/e(0)] \propto \sqrt{\mathcal{E}}$).

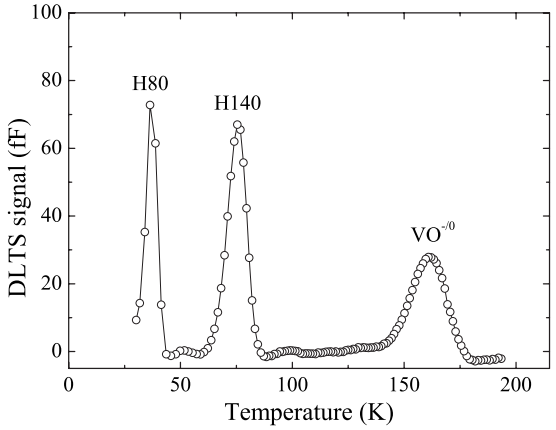

FIG. 5. A DLTS spectrum (HR sample) resulting after low-temperature (60 K) irradiation with 2 MeV electrons and subsequent heating to RT. The spectrum was measured at a rate window of 20 s^{-1} with a filling pulse from −5 to −0.1 V and a pulse duration of 1 ms.

suppressed by the low energy transfer from electrons. In fact by varying separately the proton irradiation dose and flux it was investigated if any of the peaks in Fig. 3 were due to a secondary defect (formed by association of primary defects). No definite enhancement of the defect concentration by increasing the flux was seen, and there was no quadratic trend of the defect concentration as a function of irradiation dose. A quadratic trend has been observed in *n*-type germanium previously,[17] and hence H80 and H320 do not appear to be secondary defects but rather larger primary defect complexes. The characteristics of H80 are $E_{pa}(H80)=0.076$ eV and $\sigma_{pa}(H80)=6\times10^{-14}$ cm^2 while H320 has the parameters $E_{pa}(H320)=0.324$ eV and $\sigma_{pa}=2\times10^{-15}$ cm^2. A clear Poole-Frenkel effect[27] is exhibited by the emission rate of H80 as a function of the average electric field as shown in Fig. 4. This demonstrates that it is an acceptor level and is then, in particular, not identical to the antimony-vacancy pair donor level which yields a peak at almost the same position in DLTS spectra.[22] The capture cross section of H80 is measured to have the value $\sigma_p=3.5\times10^{-15}$ cm^2 at 40 K. Due to the overlap with emission components too close in emission rate it was not possible to analyze field dependence and capture cross section of H320.

The final clue as to the nature of H80 and H190 comes from low-temperature electron irradiation. Figure 5 shows the DLTS spectrum resulting from the irradiation of a HR n^+p-germanium diode with 2 MeV electrons at 60 K and a subsequent heating to RT under zero bias before measurement. Clearly H190 is strongly reduced if present at all while H80 is now present. We suggest that H190 has been converted into H80 by the capture of a mobile defect. That this does not happen for a 2 MeV electron irradiation at RT, as demonstrated in Fig. 1, can be explained by the different charge states populated at lower temperatures. As the temperature is raised the Fermi level moves toward midgap. So if the Fermi level has crossed electronic levels in the band gap the corresponding defects will be populated by less electrons at low temperature than at RT. Hence defects are less negative at low temperature in *p*-type germanium. The lack of the conversion of H190 to H80 at RT means thus that the mobile defect in question must be negatively charged at RT. This rules out the self-interstitial since it is well established that Ge_i is positively charged in *p*-type germanium.[21,28] The vacancy in germanium on the other hand is found to be an acceptor and becoming mobile at 200 K.[21,28] For the sample used the gallium concentration is 4.4×10^{14} cm^{-3} giving at 200 K the Fermi-level position $E_F=E_v+0.15$ eV while at RT the position is $E_F=E_v+0.24$ eV. First of all this implies that the defect responsible for H190 is indeed more negative at RT than at 200 K since the energy level lies between these two Fermi-level positions. Furthermore the vacancy here becomes mobile predominantly in a negative charge state,[29] verifying that the Coulomb repulsion is stronger between the vacancy and the defect responsible for H190 at RT. It is therefore plausible that H190 is removed due to vacancy capture. In fact it is hard to imagine a mechanism preventing the formation of H190 as a primary defect at low temperature. The suggested connection between H80 and H190 implies that both are vacancy-type defects. These conclusions fit very well with the observation that H80 cannot be created directly by irradiation with 2 MeV electrons at RT. As remarked earlier gallium is not involved in H190 and it is not likely that oxygen is either since the oxygen concentration is low. Thus H190 and H80 consist only of vacancies, and the most likely candidates are therefore, respectively, the divacancy and trivacancy defects. As can be seen from Fig. 3 both of them are formed directly in a 2 MeV proton irradiation and slightly more trivacancies than divacancies are formed.

No additional emission component in the DLTS transient that could be related to H190 has been observed even at 20 K. This leaves the question as to why there is only one acceptor level of the divacancy in the band gap when two were expected from theory and $Si_{1-x}Ge_x$ experiments. The answer likely lies in a negative-*U* ordering of the two acceptor levels resulting in only one DLTS peak. As remarked earlier theory predicts the single and double acceptors to be very close. Further the actual crossing of midgap by the double acceptor has not been observed directly by DLTS in $Si_{1-x}Ge_x$, so an inverted ordering is not ruled out from those experiments

either. This suggestion implies that H190 is due to the transition $V_2^{=/0}$, behaving like a single acceptor since the emission of the first hole is the rate-limiting step. This assignment of H190 means that the divacancy is neutral at 200 K and double negative at RT explaining the ability to capture vacancies at 200 K. H80 has a rather low capture cross section for an acceptor so it is most likely a single acceptor which means it should be assigned to the transition $V_3^{-/0}$ of the trivacancy. In fact this defect has recently been observed by DLTS in silicon.[30]

If the claim that H140 is a donor level does not hold, it should be considered as a divacancy candidate as well. On the other hand, in the current picture this would force us to identify H190 with a trivacancy and H80 with a tetravacancy. This seems unlikely and hence we trust the assignment of the divacancy to H190.

Finally one may speculate that H140 is an interstitial-type defect since the similar annealing temperature with H190 could be due to the dissociation or migration of H140 causing annihilation of the divacancy. Actually an energy level of the di-interstitial defect (I_2) has recently been discovered in CVD grown *p*-type silicon.[31] Additional information is required to make a firm conclusion but we may speculate that H140 is due to the I_2 defect. It may also be that the similar annealing temperature of H140 and H190 is simply a coincidence. In that case the difference between the annealing temperature of the divacancy found in this work (415 K) and in the work by av Skardi *et al.* (525 K or higher) can be explained by the different charge states the divacancy is in during the annealing. In our case it is in its doubly negative charge state while in the experiment by av Skardi *et al.* it is primarily in the singly negative charge state.

V. SUMMARY

In conclusion, n^+p germanium mesa diodes were used to search for energy levels of the divacancy in germanium. The results strongly point to the identification of one acceptor level introduced by the divacancy which likely account for both a single and a double acceptor energy level due to an inverted ordering of the levels. Additionally the divacancy was argued to be able to capture a vacancy after low-temperature electron irradiation thus becoming a trivacancy and yielding another single-acceptor trap. It should be noted in conclusion that by using DLTS, as has been done in the present investigation, unambiguous identifications of defects are not possible, and identifications based on DLTS investigations always rely to some degree on educated speculations.

ACKNOWLEDGMENTS

Thanks are due to Pia Bomholt and John Lundsgaard Hansen for preparation of the n^+p diodes. This work was supported by the Lundbeck foundation and the Danish Natural Science Research Council.

*anl@phys.au.dk

[1] G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).
[2] B. G. Svensson, B. Mohadjeri, A. Hallén, J. H. Svensson, and J. W. Corbett, Phys. Rev. B **43**, 2292 (1991).
[3] A. N. Larsen, A. B. Hansen, and A. Mesli, Mater. Sci. Eng., B **154-155**, 85 (2008).
[4] T. P. Leervad Pedersen, A. N. Larsen, and A. Mesli, Appl. Phys. Lett. **75**, 4085 (1999).
[5] V. P. Markevich, A. R. Peaker, L. I. Murin, and N. V. Abrosimov, Appl. Phys. Lett. **82**, 2652 (2003).
[6] H. av Skardi, A. B. Hansen, A. Mesli, and A. N. Larsen, Nucl. Instrum. Methods Phys. Res. B **186**, 195 (2002).
[7] J. Weber and M. I. Alonso, Phys. Rev. B **40**, 5683 (1989).
[8] J. Coutinho, V. J. B. Torres, R. Jones, A. Carvalho, S. Öberg, and P. R. Briddon, Appl. Phys. Lett. **88**, 091919 (2006).
[9] J. Coutinho (private communication).
[10] H. Stein, in *Radiation Damage and Defects in Semiconductors*, edited by J. E. Whitehouse (Institute of Physics, London, 1973), pp. 315–321.
[11] S. R. Morrison and R. C. Newman, J. Phys. C **6**, 1981 (1973).
[12] L. Khirunenko, N. Tripachko, V. Shakhovtsov, V. Yashnik, and V. Shumov, Mater. Sci. Forum **196-201**, 167 (1995).
[13] P. Vanmeerbeek, P. Clauws, H. Vrielinck, B. Pajot, L. Van Hoorebeke, and A. N. Larsen, Phys. Rev. B **70**, 035203 (2004).
[14] F. Poulin and J. Bourgoin, Rev. Phys. Appl. **15**, 15 (1980).
[15] V. Nagesh and J. W. Farmer, J. Appl. Phys. **63**, 1549 (1988).
[16] J. Fage-Pedersen, A. N. Larsen, and A. Mesli, Phys. Rev. B **62**, 10116 (2000).
[17] V. Kolkovsky, M. C. Petersen, and A. N. Larsen, Appl. Phys. Lett. **90**, 112110 (2007).
[18] J. W. Corbett and G. D. Watkins, Phys. Rev. Lett. **7**, 314 (1961).
[19] K. Kuitunen, F. Tuomisto, J. Slotte, and I. Capan, Phys. Rev. B **78**, 033202 (2008).
[20] V. Kolkovsky, M. C. Petersen, A. N. Larsen, and A. Mesli, Mater. Sci. Semicond. Process. **11**, 336 (2008).
[21] A. Mesli, L. Dobaczewski, K. B. Nielsen, V. Kolkovsky, M. C. Petersen, and A. N. Larsen, Phys. Rev. B **78**, 165202 (2008).
[22] C. E. Lindberg, J. Lundsgaard Hansen, P. Bomholt, A. Mesli, K. Bonde Nielsen, A. N. Larsen, and L. Dobaczewski, Appl. Phys. Lett. **87**, 172103 (2005).
[23] Oxygen is present at an elevated concentration due to in diffusion from the top layer during sample growth. The extracted DLTS fingerprint of the $VO^{-/0}$ energy level is $E_{pa}=0.332$ eV and $\sigma_{pa}=1.4\times10^{-14}$ cm^2 while the capture cross section is found to have a temperature dependence given by $\sigma_p=3\times10^{-17}\times\exp(-0.031\ \text{eV}/k_BT)$ cm^2, as speculated by Markevich *et al.* (Ref. 24).
[24] V. P. Markevich, I. D. Hawkins, A. R. Peaker, V. V. Litvinov, L. I. Murin, L. Dobaczewski, and J. L. Lindström, Appl. Phys. Lett. **81**, 1821 (2002).
[25] S. D. Ganichev, E. Ziemann, I. N. Yassievich, W. Prettl, A. A. Istratov, and E. R. Weber, Phys. Rev. B **61**, 10361 (2000).
[26] M. C. Petersen, C. Lindberg, K. Bonde Nielsen, A. Mesli, and A. N. Larsen, Mater. Sci. Semicond. Process. **9**, 597 (2006).

[27] J. L. Hartke, J. Appl. Phys. **39**, 4871 (1968).
[28] H. Haesslein, R. Sielemann, and C. Zistl, Phys. Rev. Lett. **80**, 2626 (1998).
[29] There is disagreement as to whether the observed vacancy energy level is a double (Ref. 21) or single acceptor (Ref. 28). Nevertheless the most recent results (Ref. 32) regarding this energy level places it at $E_v+0.13$ eV, making the vacancy negative at 200 K regardless in our case.
[30] V. P. Markevich, A. R. Peaker, S. B. Lastovskii, L. I. Murin, J. Coutinho, V. J. B. Torres, P. R. Briddon, L. Dobaczewski, E. V. Monakhov, and B. G. Svensson, Phys. Rev. B **80**, 235207 (2009).
[31] A. N. Larsen, H. Juul Pedersen, M. C. Petersen, V. Privitera, Y. Gurimskaya, and A. Mesli (unpublished).
[32] M. C. Petersen, Ph.D. thesis, Aarhus University, 2010.