℘

Negative-U property of interstitial hydrogen in GaAs

Vl. Kolkovsky,[*] K. Bonde Nielsen, and A. Nylandsted Larsen
Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

L. Dobaczewski
Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32-46, 02-668 Warsaw, Poland
(Received 9 May 2008; published 29 July 2008)

We identify the donor level of interstitial hydrogen in GaAs, which is characterized by the activation enthalpy $E_C - E_t = 0.13$ eV. This level is the marker of two different but closely related defect structures, which are indistinguishable as far as their emission properties are concerned; however, discernible on the basis of their different dynamical behaviors are revealed by annealing studies. We interpret the two structures as regular bond center hydrogen H(BC) and bond center hydrogen H(BC'), which is perturbed by the local strain from a neighbor point defect. We demonstrate negative-U properties of the perturbed structure and infer that the corresponding acceptor H(T') lies deep in the band gap. These results for interstitial hydrogen in GaAs are in every aspect analogous to the properties of interstitial hydrogen in Si.

I. INTRODUCTION

The behavior of hydrogen in crystalline semiconductors has attracted considerable interest during several decades. Due to its high diffusion rate and ability to react with a wide variety of lattice imperfections such as intrinsic point defects, impurities, interfaces, and surfaces, hydrogen is an impurity of fundamental importance in semiconductor materials. For example, hydrogen may be embedded during crystal rinse in device processing steps typically forming bound complexes with intentional dopants and other defects passivating them and thereby modifying the electrical activity. A natural starting point for investigating the effects of hydrogen incorporation is to determine the properties of isolated H atoms interacting with a perfect semiconductor crystal. However, despite the vast amount of work on hydrogen in semiconductors, only isolated H species in the elemental materials, Si and Ge, and in SiGe alloys has been unambiguously identified.

The properties of isolated hydrogen embedded in Si are well understood.[1–3] The H impurity may exist in three different charge states H$^+$, H^0, and H$^-$ depending on which site in the crystal lattice it occupies.[2,3] These charge states give rise to either a donor level $(0/+)$ ascribed to hydrogen at the bond center site (BC) or an acceptor level $(-/0)$ ascribed to the tetrahedral interstitial site (T). The acceptor level is in some presentations[4] defined as the change in energy when hydrogen emits an electron, and as a result jumps from the T site to the BC site . This definition connects to another important feature, namely, the inverted order of the donor and acceptor levels (i.e., the negative-U property). For a negative-U system lattice relaxations overrule the Coulombic repulsion between bound carriers so that the second carrier is bound more strongly than the first one. This is in contrast to a normal defect where the second carrier is more loosely bound. For the case of hydrogen then the emission of the first electron from H$^-$(T) is followed immediately by the emission of the second electron from H^0(BC) provided that the barriers for the jump between the two sites can be neglected.

However, at low-temperature hydrogen must indeed overcome a significant barrier with the consequence that H^0(BC) is metastable rather than unstable. Furthermore the H$^-$(T) emission may initiate rapid migration of H^0 through the open interstitial areas of the Si lattice in competition with H^0 jumping into a bond center site.

It should be emphasized that the notation BC and T sites is not necessarily restricted to the sites of the undisturbed silicon lattice. It has been shown that local strain caused by nearby impurities such as interstitial oxygen,[2] substitutional site carbon,[5] or germanium[6] modifies the properties of the isolated hydrogen configurations weakly. Therefore, it is sensible to talk about perturbed versions of the BC or T sites rather than new defect structures.

Similar charge states of H and its configurations (in Ge as well) were predicted[7] and observed.[8] However, contrary to the Si case the single acceptor level of hydrogen in Ge is believed to be resonant with the valence band. In compound semiconductors such as the III-V semiconductor GaAs, the general features of the behavior of isolated H are also expected to be similar to that in Si.[7] Thus, for example, Bonapasta *et al.*[9] by analyzing the atomic arrangements and the electronic charge distributions for isolated H in the presence of a deep donor—the As$_{Ga}$ antisite defect—predicted an inverted order of the isolated H levels in GaAs. Based on this theoretical work it is inferred that the stable site of H in intrinsic GaAs is antibonded to the As site, whereas neutral H is metastable at the bond centered position. On the other hand, in p-type GaAs the stable configuration is H$^+$ at the bond center site. In n-type material H$^-$ is ascribed to the interstitial tetrahedral site in average as a result of possible jumping between antibonding sites. Until now, except for a few measurements in GaAs, there is very little direct experimental information regarding the individual isolated hydrogen states and most reported properties are inferred indirectly with assumptions as to which these hydrogen related centers may be present. The existence of the donor level of H in n-type GaAs was reported briefly in our previous work.[10] The present paper extends this work providing additional

information on diffusion and charge state properties of isolated H in GaAs. A detailed analysis of isolated hydrogen related defects generated by low-temperature hydrogen implantation in combination with *in situ* application of the high-resolution Laplace deep level transient spectroscopy[11] (Laplace DLTS) will be presented.

II. SAMPLE PREPARATION

The samples used in the present study were prepared from liquid encapsulated Czochralski-grown *n*-type GaAs crystalline material on which Schottky diodes have been formed by vacuum evaporation of gold on the polished side of the samples. The concentration of electrons at room temperature was 1×10^{15} cm^{-3} and even higher at elevated temperatures. However due to a high concentration of deep compensating defects, this reduces to around 2×10^{13} cm^{-3} at 60 K. This low carrier concentration at the measurement temperature allows hydrogen to be implanted with a range well inside the space-charge region of a suitably reverse biased Schottky diode. Supplementary crystals with very little compensation and with no carrier freeze-out were also used. These crystals had 4×10^{16} cm^{-3} electron concentration and this value stayed practically unchanged in the whole temperature range investigated. However, the high number of electrons made the Schottky junction too shallow for a direct implantation. Consequently these highly doped samples were implanted through a 1.3 μm gold foil in order to slow down the implanted atoms and make the range match the active depth of the junction. Thus, in order to obtain a reasonable strength of the DLTS signals much larger implantation doses were needed, which in turn caused a higher damage level in the crystal and more local strain. Furthermore, the higher electron concentration also means larger electric field in the space-charge region, which for a donor state makes the thermal emission rate have a spatial distribution. As a result, the Laplace DLTS peaks observed with the shallow junctions were rather broad, which made the experimental conditions less favorable. As a consequence, we used the shallow junctions only for the comparison of He and H implantations.

The samples were mounted on the cold finger of a cryocooler and implanted with protons at temperatures around 60 K. The implantation energy was chosen so that the peak of the implant matched the depletion width of the diode (around 20 μm) under suitable reverse bias at the implantation temperature. For hydrogen implantation the energy was typically 1 MeV, which for GaAs corresponds to an implantation depth of $\sim$17 μm. The GaAs samples were implanted with a series of shots up to the total dose of $\sim 3 \times 10^{10}$ cm^{-2}. All implantations were monitored *in situ* by capacitance-voltage (CV) profiling and subsequent Laplace DLTS measurements.

III. EXPERIMENT RESULTS AND ANALYSIS

A. Implantation

Figure 1 shows the depth profile of the carrier concentration derived from the CV measurements of a GaAs sample before (triangles) and after (squares and cross symbols) proton implantation. The diode was unbiased during the implan-
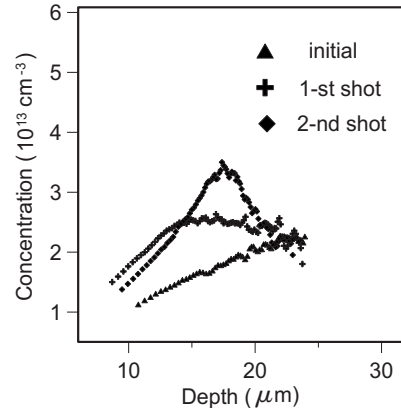

FIG. 1. Carrier concentration versus depth derived from the CV profile before (triangles) and after [squares and cross symbols (see details in the text)] implantation. The increase in the carrier profile at around 16 μm coincides with the peak concentration of protons.

tation. In this case toward the end of its slowing down a fraction of the initially positive hydrogen implants is expected to capture electrons and possibly migrate in the neutral charge state. Ultimately then, from this quasithermal environment of the collision cascade hydrogen may at low temperature end up in a bond center position as metastable H^0 or in a near-*T* site as H$^-$ upon capture of an additional electron. This picture anticipates the expected negative-*U* character and the existence of a barrier separating the H^0(BC) and H^0(T)/H$^-$(T) configurations. The total implantation dose, which corresponds to the curve shown with squares in Fig. 1, was estimated to be about 3×10^{10} cm^{-2}. The curve indicates the presence of a donor compensation caused by the implantation. However, the compensation profile is much too broad to be accounted for by the implantation straggling, giving rise to overlapping secondary vacancy and hydrogen profiles at the implantation range. Hence, it can be directly deduced from the as-implanted CV profiles that considerable migration has taken place during the implantation carried out at 60 K. Due to the overlap of vacancy and hydrogen profiles and a possible counter compensation from H$^-$, one cannot deduce the number of H$^+$ implants directly from the shallow donor compensation profile. However, a clear increase in the donor concentration is observed at around the implantation range of 16 μm.

Figure 2 depicts typical Laplace DLTS spectra recorded at 65 K for the GaAs sample implanted in succession with increasing doses of protons. As seen in the figure, the amplitude of the dominant line at the emission rate of 10 s^{-1} increases as a function of the proton dose. After the total irradiation dose of around 3×10^{10} cm^{-2}, a sharp dominant line is observed [Fig. 2(c)]. This line clearly indicates a monoexponential transient related to a single well defined energy level. Using Arrhenius analysis, this level is characterized by the activation enthalpy of emission $E_C - E_t$ =0.13 eV and a pre-exponential factor equal to 5.5 $\times 10^7$ s^{-1} K^2. The defect concentration corresponding to this Laplace DLTS peak was evaluated to be $\sim 10^{13}$ cm^{-3} and, thus, at least the main part of the donor compensation indicated in Fig. 1 most likely stems from this defect. Further-
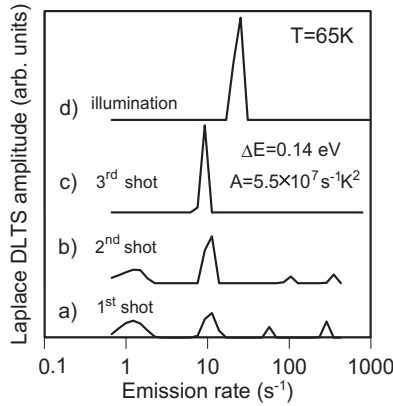
FIG. 2. Laplace DLTS spectra recorded at 65 K in proton irradiated GaAs to different doses (a), (b), and (c). The spectrum in (d) is taken after subsequent illumination of the proton irradiated sample for 30 s.

more, direct profiling of the DLTS signal shows that this signal originates from the same depth region as the CV profiles shown in Fig. 1 and is similarly broadened. However, the signal accounts only for about 15% of all implanted hydrogen. This experimental fact in combination with the observed broadening of the compensation profile strongly suggests that the migration during implantation also leads to the trapping of hydrogen in unknown mostly neutral defect structures. It is important to note that no signals have been observed at the measurement temperature prior to the proton implantation. Furthermore, hydrogen and helium implantation were compared with the noncompensated samples for doses leading to a similar damage level in the two cases. The absence of a peak at the emission rate of ~ 10 s^{-1} for the He-implanted sample shows unambiguously that this recorded emission peak is related to hydrogen.

This assignment to hydrogen can be corroborated with the conventional DLTS scans carried out. The conventional DLTS spectra recorded for as-grown (solid line) and proton irradiated (dashed line) GaAs are shown in Fig. 3. In the as-grown sample two dominant peaks are observed at around 170 and 270 K. These peaks have been earlier assigned to

EL5 and EL3. The EL5 defect is associated with the Ga-As vacancy complex, V_{Ga}-V_{As},[12] while the microscopic structure of EL3 was determined as off center substitutional oxygen on the arsenic site, O_{As},[13,14] Besides the two dominant peaks shown in Fig. 3, minor features—labeled EL6 and EL7 in the present work—were detected in the DLTS spectrum. EL6 is believed to be the complex As antisite (As vacancy, As_{Ga}-V_{As})[12,15] whereas the EL7 defect is unidentified. It should be noted that increasing the temperature above 330 K allows the EL2 midgap level to be observed. The arsenic antisite (As_{Ga}) is generally accepted to be the most realistic model, which describes its structure.[16] Due to the very high intensity of EL2, which is about three times higher than the dominant lines of the spectra, the content of the figure is limited to the temperature range below 300 K. The introduction of hydrogen results in an intensity increase in the EL5 and its left side satellite EL6. Additionally, a new peak denoted H$^{+/0}$ is observed at around 65 K. A comparison of the intensity and position of H$^{+/0}$ with the line observed in the Laplace DLTS spectrum [Fig. 2(c)] shows that both of them represent the same defect.

FIG. 4. The normalized change in concentration of the trap responsible for the dominant line seen at the emission rate of 30 s^{-1} at 65 K in the Laplace DLTS spectrum upon 15 min isochronal annealing steps. The bias was off during each step.

B. Annealing studies

The normalized changes in intensity of the H$^{+/0}$ trap upon 15 min isochronal annealing are shown in Fig. 4. The diode was unbiased during each annealing step. Therefore, at low temperature the level H$^{+/0}$ is occupied with an electron. As seen in Fig. 4 the annealing consists of two main stages. The first one occurs within the range of 60–110 K. In this range a drop of about 70% in the intensity of H$^{+/0}$ is found. No significant difference between bias-off and bias-on annealing has been observed for this low-temperature stage. In the range of 110–450 K the amplitude that remains in the H$^{+/0}$ line first increases to almost 50% of its initial value and after that stays essentially constant until the second stage of annealing sets in, starting from 450 K. It should be emphasized that the increase in H$^{+/0}$ shown in the figure at ~ 200 K was absent for implanted samples exposed to light at 60 K prior to the annealing. The remainder of the H$^{+/0}$ defect anneals
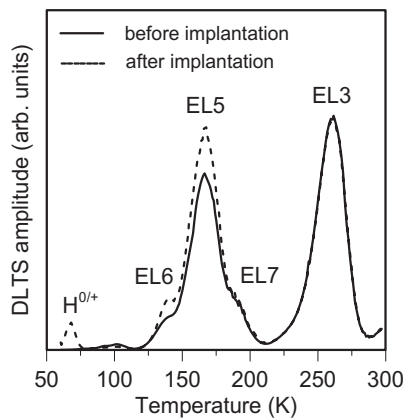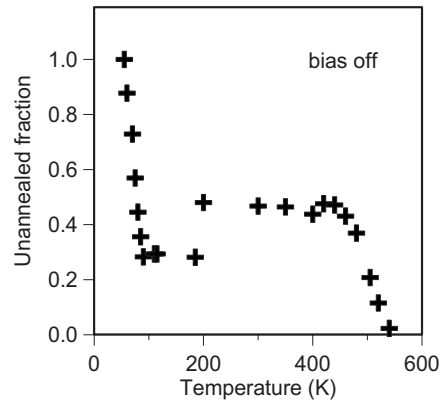

FIG. 3. Conventional DLTS spectra for as-grown (solid line) and proton irradiated (dashed line) GaAs recorded with the following parameters: $e_n = 20$ s^{-1}, $V_R = -5$ V, $V_P = -0.5$ V, and $t_p = 1$ ms.

completely at about 530 K. Because the Fermi level at the temperature of the second annealing stage must be below the level energy, it is reasonable to assume that the annealing actually occurs in the positive charge state of the defect. Hence, for the neutral state we can only claim that it anneals above the temperature where the Fermi level crosses the level position. Similarly for bias-on annealing the $H^{+/0}$ remainder stays constant up to 350 K. However, due to experimental difficulties, we could not follow the reverse bias annealing to higher temperatures. In view of the expected bias independence of the charge state in this temperature range this seems unimportant.

Until the second stage of the annealing, the full initial $H^{+/0}$ signal can be recovered by light illumination at about 60 K. This procedure can be cycled with no loss of the total signal. However, as seen in Fig. 1(d) the recovered peak is shifted to a higher emission rate and its intensity is increased to about 15% as compared to the as-implanted signal. We ascribe this shift to an artifact linked with the presence of the strong EL2 midgap signal in our GaAs samples. During some minutes this signal gradually shifts back to its original position at the emission rate of 10 s^{-1}. The shift occurs collectively, i.e., the position of the peak moves back to the original position without the broadening of its shape. Hence, it can be ruled out that a conversion between two similar defect configurations could be responsible for the shift. A peculiar characteristic of the EL2 defect is the existence of a metastable configuration of this defect, which upon illumination with light can give rise to metastable photoconductivity thereby influencing the number of electrons in the depletion layer of the Schottky diode. We conjecture that reverse bias, decay leakage photocurrent generates impact ionization and thereby causes the shift in emission rate. This conclusion is corroborated by the observation that for some diodes a similar shift has been observed when comparing signal positions for different bias settings during measurement. The low bias positions of the peak were shifted toward faster emission rates. This may likewise be ascribed to an increase in leakage current. For the heavily compensated material we assume that the impact ionization overrules the weak Poole-Frenkel shift to be expected for the donor signal.

The increased intensity of the recovered peak compared to the intensity just after implantation indicates that the illumination picks up some hidden interstitial hydrogen and transfers it to the $H^{+/0}$ configuration. Finally, it is important to emphasize that no further changes in the intensity of the first recovered $H^{+/0}$ signal were observed after subsequent annealing and repeated recovery by illumination.

As seen in Fig. 3 the introduction of hydrogen into the samples does not lead to the appearance of any other peaks observed during the temperature scan, except for the one which was assigned to the donor state of interstitial hydrogen. The change in the intensities of EL5 and EL6 seen in Fig. 3 may be explained as a result of the creation of an additional number of these defects—as, for example, primary defects during the hydrogen implantation. Indeed, in this case a great number of nonequilibrium vacancies are injected into the crystal—which can interact, for example, with the As$_{Ga}$ defect forming EL6 or with V_{Ga} creating EL5. This can be the case here. However, it cannot be ruled out that for

instance the increase at the EL5 position may account for the missing hydrogen, for example, in the form of a vacancy related dangling-bond state of similar structure as EL5. One should note also that no changes in the intensity of the dominant peaks and their minor satellites were observed after annealing at room temperature when, as explained above, the loss of the $H^{+/0}$ hydrogen signal is about 70%. This clearly indicates that the $H^{+/0}$ hydrogen does not interfere with the defect structures responsible for the dominant peaks.

C. Negative-*U* property

As mentioned in the introduction we anticipate the existence of an acceptor level associated with hydrogen occupying the *T* site and a donor level associated with hydrogen occupying the *BC* site. Together these levels form a negative-*U* system in the phenomenological sense that the donor level lies above the acceptor level in the band gap. The two defect configurations may relax into one another, which is controlled by the charge attached to the hydrogen impurity. However, in contrast to an ordinary negative-*U* system the associated swing of hydrogen between the two positions in the GaAs lattice involves a significant barrier, which at sufficient low temperature allows the coexistence of $H^0(BC)$ and $H^-(T)$ in *n*-type material. This property forms the basis for the measurement described below.

It should be emphasized that there is no direct indication for the existence of the acceptor level in the conventional DLTS spectra recorded after the implantation (Fig. 3), which suggests that such level lies deeper in the band gap hidden for the DLTS measurements. The acceptor and donor levels of isolated hydrogen are anticipated from theory[7,9] to form a negative-*U* system. However, no unambiguous experimental evidence for that has been obtained so far. In order to demonstrate the negative-*U* property, as described above, we shall examine the correlation between the amounts of charge bound as H^+ and H^-. A key point for this is the property of the $H^{+/0}$ signal that can be recovered by illumination, which for a biased diode we may interpret as a direct conversion from the $H^-(T)$ state to $H^+(BC)$. When this is the case it is expected that the change in the capacitance, as a result of the light excitation of the electrons bound in the hypothetical acceptor state $H^-(T)$ and the subsequent swift relaxation into $H^+(BC)$, should be a factor of two that is larger than the change resulting from the carrier emission of the associated metastable donor state $H^0(BC)$. On the other hand, this ratio should be equal to one for the positive-*U* system when the acceptor level lies closer to the conduction band than does of the donor level. Thus, for different intensities of the signal $H^{+/0}$ as measured by Laplace DLTS after regeneration by illumination and partial annealing, we obtain a set of values of the transient capacitance amplitudes relative to the saturation value. These different values are denoted as ΔC_{LDLTS} and compared in Fig. 5 to the corresponding values ΔC_{CV} of the change in total capacitance when the sample is illuminated to recover the initial $H^{+/0}$ signal for each pertinent DLTS recording. The same reverse bias voltage was applied in both sets of measurements. As seen in the figure, a perfect linear correlation with a slope of two is revealed between the
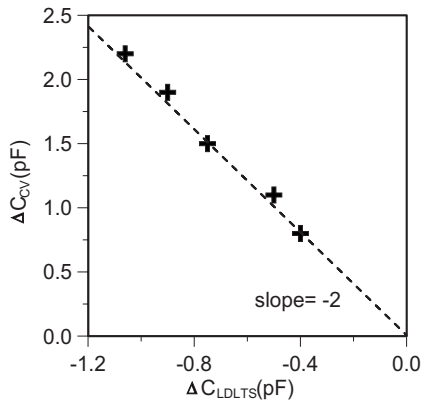
FIG. 5. The change in the total capacitance of the GaAs sample caused by illumination as a function of the corresponding change in the transient capacitance observed by Laplace DLTS measured before and after the illumination.

two ΔC sets. We take this as an unambiguous proof of the negative–U property of interstitial hydrogen in GaAs. It should be noted, however, that this statement refers only to the part of $H^{+/0}$ that anneals in the first stage. The precursor for the recovery of $H^{+/0}$ anneals at ~450 K indicating that the acceptor level lies very deep in the band gap, presumably in a lower half, because we have to assume that the annealing is initiated by thermal electron emission. Now in perfect analogy with a similar result for Si[3], one can suppose that $H^{+/0}$ in reality consists of two signals stemming from a perturbed and unperturbed form of bond center hydrogen. The experimental fact that the part of the $H^{+/0}$ signal belonging to the first annealing stage can be recovered repeatedly with no loss in amplitude strongly suggests that this part originates from a hydrogen defect, which is locked in the GaAs crystal by local strain. Otherwise successive illuminations would cause additional broadening of the implantation profile and eventually lead to removal of hydrogen from the depletion layer. As a natural consequence of this conclusion, we assign the rest of the $H^{+/0}$ signal to the regular bond center position of hydrogen. It is remarkable then that we are dealing with two types of defects, which can be discerned by their different dynamical behavior but so close in level energy that they appear in the DLTS measurements as the same defect. As stated above these finding are very analogous to the situation in silicon, which we shall lean heavily on in the discussion section below.

IV. DISCUSSION

The results and analysis presented in the previous sections strongly favor the assignment of the $H^{+/0}$ signal in the Laplace DLTS spectrum to two independent but very similar donor states of interstitial hydrogen. Moreover, combining the experimental findings with the theoretical predictions, we conclude that hydrogen occupies a bond center type configuration in both cases. It was shown in Ref. 2 that in an oxygen-rich hydrogen-implanted silicon diode up to 80% of the implants is initially embedded as H(*BC*) and the rest as H(*BC*)-O_i depending on the implantation conditions. In this

case the initially observed donor profile was much sharper than the present CV data for GaAs. This is consistent with the result that in the present case only about 15% of the implants are embedded in the bond center configuration just after implantation. In fact the experimental analogy goes much further as already mentioned. The H(*BC*)-O_i defect in Si anneals at very low temperature in the neutral charge state. It is, however, stable in the positive charge state and can be completely recovered at low temperature under reverse bias illumination just as $H^{+/0}$ in the present investigation. Furthermore, the negative-U property of hydrogen in Si has been revealed in the same way as in the present work. Hence, it is perfectly possible that this analogy can be extended even further to assume that the fraction of $H^{+/0}$, which anneals at low temperature, likewise originates from a bond center configuration, which is strained by neighboring interstitial oxygen, whereas the fraction that survives room-temperature annealing originates from a regular unperturbed bond center configuration. Hereafter, the perturbed and unperturbed fractions of $H^{+/0}$ are denoted as H(*BC*) and H(*BC'*), respectively. First we shall discuss the H(*BC*) configuration.

Using the infrared (IR) absorption technique, Stein *et al.*[17] observed local vibrational modes (LVM) that indicates the preference of chemical bonding of hydrogen to both the As and Ga host constituents of GaAs following hydrogen implantation at 80 K. In contrast to this the room-temperature implantation of hydrogen leads to the appearance of local vibrational modes only from the Ga-H bonds, whereas the modes originating from the As-H bond are absent. Hence, for low-temperature implantation, an apparent preferential formation of As-H bonds was observed. This tendency was explained by lattice strain and selective bonding on defects produced on the Ga sublattice that exposes weak As dangling bonds capturing hydrogen.

It is tempting to correlate the survival in the IR studies of the Ga-H signal to above room temperature with H(*BC*) ascribed to the regular bond center position in the present work. The formation of Ga-H centers was investigated in details in Ref. 17. It has been concluded that after a low-temperature implantation these complexes are predominantly formed during subsequent annealing of unstable As-H centers between 180 and 250 K. Hydrogen atoms, which are released during this annealing, were concluded to be available for retrapping by Ga. This experimental result is consistent with theoretical findings,[18] which predict that bond centered hydrogen in GaAs forms a stronger bond with a Ga neighbor because of its lower electronegativity (3.28) when compared with the electronegativity of an As neighbor (3.9) in an undamaged lattice. This conclusion is further supported by the fact that the small differences in the atomic masses, bond energies, and bond dissociation energies of Ga and As play a minor role.[19,20]

The identification in the present work of the surviving fraction of the $H^{+/0}$ signal as H(*BC*) is in accordance with the conclusions obtained from the IR data. With this identification H(*BC*) may be correlated with the 1834-cm^{-1} band assigned to a stretch mode for Ga-H bonds when it is assumed that bond center hydrogen form a much stronger bond with Ga than with As. Moreover, this assignment is consistent

with the increase in the intensity of the H$^{+/0}$ line at about 200 K by up to 50% of its initial value as shown in Fig. 4. This increase is believed to be due to the release of hydrogen from hidden centers invisible to the capacitance techniques. However, since the increase does not influence the ability to recover the H(BC') by illumination, one can conclude that the source for the increase is not linked with the annealing of the precursor for this defect, rather the connection between the two fractions of H$^{+/0}$ and/or their precursors is related to the competition in their formation during implantation and subsequent illumination.

As for the nature of the H(BC') structure, one can speculate that the annealing H(BC')→H(T') of the unstable fraction of H$^{+/0}$ results from a jump of hydrogen from the bond center Ga-H position to an interstitial T site opposite to the antisite (As$_{Ga}$), i.e., to a structure As$_3$As-H where a Ga neighbor was replaced by As. If this is the case, the parent defect H(BC)-As$_{Ga}$ can be chosen as a possible alternative to the H(BC)-O$_i$ found in Si. The possible existence of such an antisite perturbed hydrogen defect has been proposed to explain the formation of a dominant 2029-cm^{-1} band in the IR spectrum of GaAs after implantation at 80 K. During the implantation of hydrogen, multiple displacements of atoms from their regular periodic positions take place. It is believed that the As-H bonds form at As vacancy (V_{As}) or Frenkel pair (V_{As}-A$_{si}$) displacement defects on the As sublattice.[21–24] Similar conclusions have been made using DLTS studies.[25] However, the Ga vacancy centers (V_{Ga}), which are expected to be a dominant defect in implanted crystals have never been observed. This indicates that this defect is mobile below room-temperature forming, for example, As$_{Ga}$As$_3$-V_{As} complexes.[26] Stein *et al.*[17] suggested that V_{As} in these complexes can interact with hydrogen forming As$_3$As-H defect, which is perturbed by the presence of As$_{Ga}$. This defect structure would be identical to the one proposed above.

However, if we are indeed dealing with the same defect in these two cases, we should explain why their annealing properties are so different. In the DLTS study the defect is stable for heating up to about 450 K, at which temperature H(BC') can no longer be recovered. In contrast to this the 2029-cm^{-1} band disappears completely at room temperature. This apparent inconsistency might be related to the extreme difference in the hydrogen doses in the two cases ($\sim 10^{13}$ and $\sim 10^{18}$ cm^{-3}, respectively). In the IR samples the Fermi level will be pinned near midgap and this might force hydrogen out of the negative charge state at a much lower temperature than in the DLTS case. This may in turn cause annealing and migration eventually leading to formation of H(BC), as would be indicated by the increase in the 1834-cm^{-1} band assigned tentatively to this defect.

It should be emphasized that the possibility of assigning H(BC') to H(BC)-As$_{Ga}$ relies on the availability of enough antisites to compete with possible trapping of oxygen. As

mentioned previously the crystal used in the present work is strongly compensated with the EL2 defect, and because of the strong compensation it is not possible to evaluate properly the concentration of EL2 from the conventional DLTS spectrum. Moreover, assuming that the structure of EL2 consists of As$_{Ga}$, the signal is so much stronger than the hydrogen signals in which it is not possible to detect a drop in the abundance of this center caused by the trapping of hydrogen.

Finally, we address the experimental result that only about 15% of implants enter the bond centered position during the low dose implantations and only a minor increase is achieved by subsequent illumination. This means that immediately after the implantation very little hydrogen is present as H(T')—which, from the annealing and negative-U measurements, are shown to act as precursors for the formation of H(BC'). It is not likely either that any significant amount of hydrogen is present at the regular T sites because illumination does not cause an increase in H(BC). As a consequence, one can assume that about 80% occupy electrically inactive defect structures. It is, however, possible that hydrogen combines with vacancies generated during the implantation and forms dangling-bond structures with electrical properties similar to the EL5 defect. Hence, the increase in the position of the EL5 line observed could be hydrogen related but the increase could of course also be caused by the implantation generated vacancies themselves.

V. SUMMARY

To conclude we have identified a donor level of interstitial hydrogen in GaAs, which is characterized by an activation enthalpy of emission $E_C - E_t = 0.13$ eV and a pre-exponential factor equal to 5.5×10^7 s^{-1} K^2. The level refers to two different defect structures, which are indistinguishable as far as their emission properties are concerned, but could be discerned on the basis of their different dynamical behaviors. We have ascribed the two structures to regular bond center hydrogen H(BC) and bond center hydrogen H(BC'), which is perturbed by the local strain from a neighbor point defect. The As$_{Ga}$ antisite is considered as one of the plausible candidates for the perturbing defect. We have demonstrated the negative–U properties of the H(BC')/$H(T')$ system and inferred from the annealing properties that the corresponding T'-site acceptor level H$^{0/-}$(T') lies deep in the band gap. The results obtained are in every aspect similar to the properties of isolated hydrogen in Si. Analog annealing stages have been identified although the actual values of barriers differ considerably.

*vk@phys.au.dk

[1] See review by S. K. Estreicher, Mater. Sci. Eng., R. **14**, 319 (1995), and references therein.

[2] K. Bonde Nielsen, B. B. Nielsen, J. Hansen, E. Andersen, and J. U. Andersen, Phys. Rev. B **60**, 1716 (1999).

[3] K. Bonde Nielsen, L. Dobaczewski, S. Søgård, and B. Bech Nielsen, Phys. Rev. B **65**, 075205 (2002).

[4] C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. B **39**, 10791 (1989).

[5] O. Andersen, A. R. Peaker, L. Dobaczewski, K. Bonde Nielsen, B. Hourahine, R. Jones, P. R. Briddon, and S. Ôberg, Phys. Rev. B **66**, 235205 (2002).

[6] K. Bonde Nielsen, L. Dobaczewski, A. R. Peaker, and N. V. Abrosimov, Phys. Rev. B **68**, 045204 (2003).

[7] C. G. Van de Walle and J. Neugebauer, Nature (London) **423**, 626 (2003).

[8] L. Dobaczewski, K. Bonde Nielsen, N. Zangenberg, B. Bech Nielsen, A. R. Peaker, and V. P. Markevich, Phys. Rev. B **70**, 079901(E) (2004).

[9] A. Amore Bonapasta, M. Capizzi, and P. Giannozzi, Phys. Rev. B **57**, 12923 (1998).

[10] L. Dobaczewski, K. Bonde Nielsen, A. Nylandsted Larsen, and A. R. Peaker, Physica B **376-377**, 614 (2006).

[11] L. Dobaczewski, A. R. Peaker, and K. Bonde Nielsen, J. Appl. Phys. **96**, 4689 (2004).

[12] T. Wosinski, A. Makosa, and Z. Witczak, Semicond. Sci. Technol. **9**, 2047 (1994).

[13] M. Skowronski, S. T. Neild, and R. E. Kremer, Appl. Phys. Lett. **57**, 902 (1990).

[14] U. Kaufmann, E. Klausmann, J. Schneider, and H. Ch. Alt, Phys. Rev. B **43**, 12106 (1991).

[15] Z. Q. Fang and D. C. Look, Appl. Phys. Lett. **63**, 219 (1993).

[16] E. R. Weber, H. Ennen, U. Kanfmann, J. Windschief, J. Schneider, and T. Wosinski, J. Appl. Phys. **53**, 6140 (1982).

[17] H. J. Stein and J. C. Barbour, Phys. Rev. B **56**, 3813 (1997).

[18] S. K. Estreicher, Mater. Sci. Forum **148-149**, 349 (1994).

[19] J. R. Creighton, J. Vac. Sci. Technol. A **8**, 3984 (1990).

[20] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, London, 1986), p. 270.

[21] B. Pajot, B. Clerjaud, and J. Chevallier, Physica B (Amsterdam) **170**, 371 (1991).

[22] R. C. Newman and J. Woodhead, Radiat. Eff. **53**, 41 (1980).

[23] J. Tatarkiewicz, A. Krol, A. Breitschwerdt, and M. Cardona, Phys. Status Solidi B **140**, 369 (1987).

[24] L. P. Wang, L. Z. Zhang, W. X. Zhu, X. T. Lu, and G. G. Qin, Phys. Status Solidi B **158**, 113 (1990).

[25] D. Pons, Physica B & C **116**, 388 (1983).

[26] H. J. von Bardeleben, J. C. Bourgoin, and A. Miret, Phys. Rev. B **34**, 1360 (1986).