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Effect of ion-gun hydrogenation on the photoluminescence of degenerate *n*-type GaAs:Si

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Hydrogenation of degenerate *n*-type GaAs:Si affects the gallium-vacancy energy levels, as observed from the optical emission of the gallium-vacancy–silicon-donor complex. The photoluminescence spectrum is modified by the activation of new states of charge for the vacancy, as a consequence of H trapping at the dangling bonds. The results allow a reinterpretation of earlier data published in the literature. In a parallel study, the near-band-gap emission is investigated to monitor the degree of passivation of Si impurities occurring upon hydrogenation of the material. A maximum figure of passivated donors of order $\frac{3}{4}$ is estimated.

I. INTRODUCTION

The optical emission spectra of highly doped semiconductors—as widely employed in the construction of emitting devices—differ from the nondegenerate material by at least two major counts: first, the near-edge free- and impurity-bound exciton lines merge into a comparatively broader emission, involving at one end of the transition the impurity-related continuous tail of states and, at the other end, levels more or less perturbed by the high impurity density. Because of the metallic character of the degenerate band, emission can take place appreciably above the fundamental edge (Burstein-Moss shift). Second, the high concentration of dopant impurities allows the formation of complexes with deep-lying impurities or defects, within which radiative transitions are possible ("internal" transitions).

The most well-known example of such an optical activation of deep centers in GaAs is offered by donors in nearest-neighbor position to the gallium vacancy (V_{Ga}), e.g., Te,[1,2] or next-nearest-neighbor position, e.g., Si.[2] Transitions within the complex give rise to a broad band, e.g., ~115-meV full width at half maximum (FWHM), and ~1.21-eV peak position for Te at 20 K.[1] The temperature dependence of the emission intensity I and of the FWHM, are found[2] to be those predicted by the configurational coordinate (CC) model, i.e.,

$$\mathrm{FWHM} = A[\coth(h\nu/2kT)]^{1/2}\ , \tag{1a}$$

$$I = I_0 \exp(E_a/kT)\ , \tag{1b}$$

where (1b) applies in the vicinity of the quenching temperature, E_a is the deactivation energy, and $h\nu$ is an effective phonon energy characterizing suitable vibrational levels of the complex. Contrary to the results of Queisser and Fuller,[1] for Te Williams reports a much larger value of A, namely ~170 meV, valid for all donors investigated.[2] The peak position at liquid-nitrogen temperature is for all donors ~1.2 eV, in particular 1.18 eV for Si and 1.21 eV for Te. The fitting energy $h\nu$ in Eq. (1a) is typically 22 meV, the quenching temperature around 200 K.[2]

We have recently demonstrated that hydrogen, incorporated in unintentionally doped *p*-type material having gallium vacancies, not only passivates deep defects and shallow acceptors,[3] but also plays—for heavy H treatments—the same role as donor impurities in the V_{Ga}-donor complex, activating a D^+-A^- "internal" transition.[4] The formation of a donor by H—with a larger binding energy than usual donors—is predicted theoretically for H trapped at the Ga-As bond center (BC).[5,6] Moreover, we have shown that, because of the possibility for H of being trapped at bonds within the V_{Ga}, more than one state of charge of the vacancy can become radiatively active.[4] In particular, states giving rise to partially overlapping emission bands at 1.14 and 1.24 eV were detected, the latter mainly at high temperature or high levels of excitation. They were, respectively, attributed to the V_{Ga}^{3-} and V_{Ga}^{2-} states, the former corresponding to the "bare" vacancy, the latter—in a simple chemical picture without lattice relaxation—conceivably to one H atom inside the V_{Ga}. One third complex seems to be possible, with two H's trapped at a dangling bond and a third one still in an adjacent bond-center position.[6] A third band observed at 1.32 eV, or slightly higher, was associated with such a complex, conceivably in the V_{Ga}^{1-} state of charge, though such assignment is still tentative.[7]

With the present paper, we intend to show that the incorporation of hydrogen in degenerate *n*-type GaAs, while shifting the material properties towards the nondegenerate condition—as shown by clearcut changes in the near-edge emission—is duly accompanied by the evolution of the V_{Ga}-related band from the one characteristic of the bare V_{Ga}-Si complex to that of the hydrogenated V_{Ga}-Si complex. Finally, in order to rule out the possibility that the observed effects are related to the creation of new defects, we shall demonstrate that the hydrogenated material can be cycled back to the virgin condition by annealing at temperatures of order 450 °C.

II. EXPERIMENTAL PROCEDURE

The material was liquid-encapsulated Czochralski-grown *n*-type GaAs, nominally Si-doped to 1.2×10^{18} cm^{-3}—with heavy compensation—purchased from

Crystal Specialties Ltd. Hydrogenation was produced by ion-beam irradiation at a temperature of 300 °C from a Kaufman-type source, with ion energy of 100 eV and current density of 40 μA/cm^2. Penetration into the bulk occurred by diffusion. Different H doses were obtained by varying the duration of the treatment. Secondary-ion mass spectroscopy in deuterated GaAs (Ref. 4) is indicative that a deuterium density comparable to the main binding impurity present is readily achieved over a depth of micrometers; longer treatments result in a deeper and deeper penetration, with moderate changes in the bulk density value, showing that the H solubility is basically set by those H-trapping defects which are most abundant. In the present experiment, the impurity having the highest concentration is silicon: we expect therefore that the concentration of H in the optically excited region be of order 10^{17}–10^{18} cm^{-3}, consistent with the near-edge spectral changes observed.

Photoluminescence (PL) measurements were made over a wide range of temperatures—2–250 K—using an Ar^+ laser as a pump. After monochromatization, the emitted light was revealed, for different levels of excitation and photon-energy regions, using a Ge detector or a Hamamatsu photomultiplier, then normalized to the overall response of the optical system. The spectral resolution, when needed, was as high as 0.3 meV.

Unless otherwise specified, we present hereafter spectra for one particular sample, referred to as sample H, corresponding to a dose of 2×10^{18} H ions impinging on the surface per cm^2. Comparison will be made with the untreated virgin material, called the *V* sample. Samples with lower H doses show a gradually evolving intermediate behavior, thus differing basically from unintentionally doped *p*-type material,[4] where the main V_{Ga}/H-donor related bands make a sudden appearance at very high levels of hydrogenation. This point is of major importance: since transitions terminating at the Ga-vacancy levels require the existence of compensating donors, this provides direct evidence of donor states related to H in *p*-type GaAs.

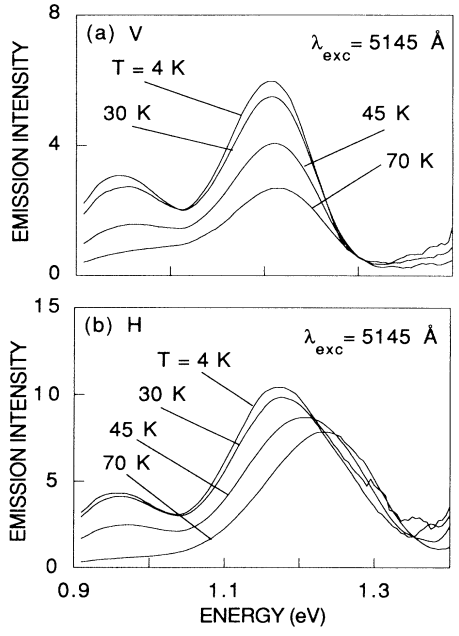

FIG. 1. The low-energy photoluminescence bands as a function of temperature between 4 and 70 K. (a) Virgin sample; (b) hydrogenated sample. Laser exciting power $P=25$ W cm^{-2}.

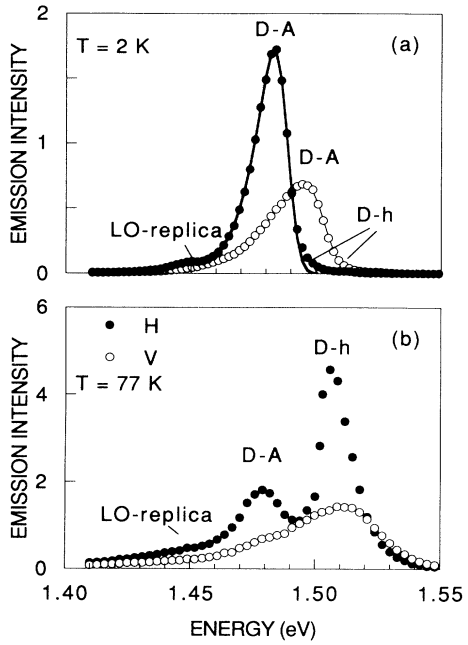

FIG. 2. (a) Detail of the edge region at 2 K: dots are experimental points, solid lines are best fitting curves for degenerate Si-donor band-to-acceptor transitions, as calculated from Eq. (2) in the discussion. Laser exciting power $P=25$ W cm^{-2}. (b) Detail of the experimental spectrum in the edge region at 77 K. Laser exciting power $P=2.5$ W cm^{-2}.

Figures 1(a) and 1(b) give the low-energy PL spectra, for argon excitation, of the virgin and hydrogenated samples, respectively, at various temperatures. The near-edge emission at 2 and 77 K, meant for an analysis of the degree of Si passivation, is correspondingly given in Figs. 2(a) and 2(b).

III. CLOSE EXAMINATION OF THE DATA

It is convenient to examine first the high-energy range. At 2 K—band-gap value 1.5193 eV, Fig. 2(a)—the virgin sample is characterized near band gap by a Burstein-Moss upward-shifted single peak at 1.495 eV, 25-meV wide at half maximum. Hydrogen passivation of a good fraction of the Si donors—which occurs whenever H is trapped near Si in an antibonding position—narrows the structure to half its original value, lowering the peak to 1.485 eV, virtually the energy of the Si-donor to Si-acceptor transition.[8] No free-exciton emission is seen, but a LO-phonon replica of the main peak is brought in clearer view, as well as a weak donor-hole emission at 1.513 eV. It should be stressed that the near-gap in-

tegrated emission for sample H, despite the deactivation of a fraction of the Si donors and of the Si acceptors, has nearly doubled, indicating an efficient passivation of deep nonradiative centers.

The 77-K data—band-gap value 1.508 eV, Fig. 2(b)—are even more meaningful, showing for sample V the Burstein-Moss-shifted transition to free holes from a mixture of donor plus free-electron states, peaking at 1.512 eV, and the parallel one to Si acceptors as a shoulder at 1.480 eV. The hydrogenated sample H shows again a contraction of the Burstein-Moss shift and a clear separation between the donor-to-valence band and donor-to-acceptor transitions, peaking at 1.506 and 1.478 eV, respectively.

The low-energy range, Fig. 1, is characterized, in the virgin material, by two deep transitions, β at 0.96 and α at 1.16 eV at 4 K. The two bands are separately analyzed by deconvolution into Gaussians. Both appear insensitive to laser power over a wide interval, indicating that a high density of levels is involved in the transitions. The β band is not of interest in this discussion—the temperature dependences of its strength and FWHM are basically different from Eqs. (1)—and it is possibly associated with clusters of silicon atoms.[9] The α band corresponds to transitions within the V_{Ga}-Si donor complex. These attributions are supported by the observation of similar bands, not reported here, in an n-type GaAs sample ($[Si]\sim 10^{19}$ cm^{-3}) where the presence of 2×10^{18} cm^{-3} V_{Ga}/Si_{Ga} complexes has been ascertained by far-infrared absorption.[10] The temperature dependences of the integrated intensity and FWHM of our α band for the virgin sample V are plotted in Figs. 3(a) and 3(b), empty dots, and compared with the same parameters after sample hydrogenation, full dots. For the V sample, the FWHM follows Eq. (1a) with $A=126$ meV, $h\nu=11.5$ meV, more in agreement with the V_{Ga}-Te behavior reported by Queisser and Fuller[1] than with the A and $h\nu$ parameters, common to all donors, given by Williams.[2] The data of Fig. 3(a) do not allow a reliable determination of the deactivation energy E_a in Eq. (1b). It is possible, however, to identify a quenching temperature of about 200 K. According to a tight-binding calculation[11] and to our analysis for p-doped GaAs,[4] this level should correspond, in equilibrium, to a 3^- charge for the vacancy.

The incorporation of hydrogen broadens the α band and shifts it upwards in energy, these effects becoming more conspicuous above 40 K. The temperature dependences of the integrated intensity and of the FWHM have changed, as shown in Fig. 3 by the full dots. The fitting of the linewidth by Eq. (1a) is not so satisfactory as for sample V, yielding now $A=180\pm 10$ meV, $h\nu=18\pm 1$ meV, values which are large and similar to those reported by Williams.[2] The quenching temperature is again around 200 K.

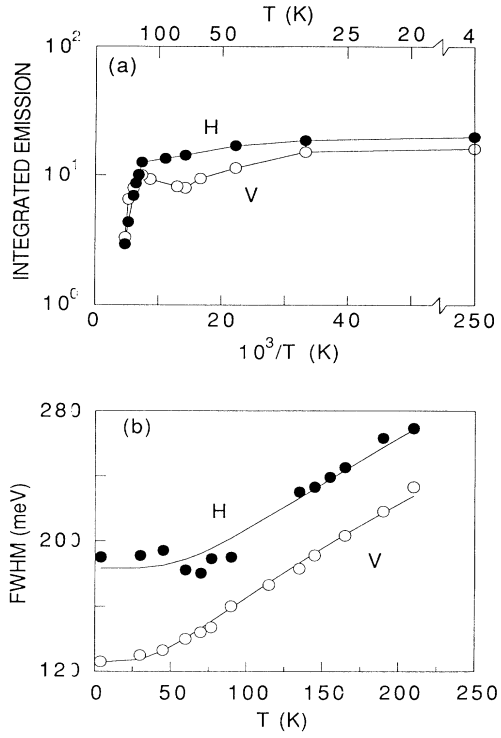

FIG. 3. (a) Integrated intensity of band α vs temperature for the virgin sample V and the hydrogenated sample H. Solid lines are guides for the eye. (b) FWHM of band α vs temperature for the virgin sample V and the hydrogenated sample H. Best fittings in terms of Eq. (1a) are shown by the continuous lines. Laser exciting power $P=25$ W cm^{-2}.

IV. DISCUSSION

A. The near-gap range

The pronounced asymmetry of the 1.495-eV emission band at 2 K in the virgin sample—see Fig. 2(a)—is indicative of transitions which do not obey the momentum selection rule, even if transitions to the continuum are concerned.[12,13] The width of the emission for the degenerate donor-to-acceptor transition is defined therefore by the bottom of the Si-impurity-band tail and the Fermi level E_F for the degenerate electron gas. Some broadening is added by the Gaussian line shape of the acceptor states, resulting from high-density effects.[12] Assuming for the conduction states, down to include the Si-donor band, the density function $\rho(E,\eta)$ calculated by Kane[14] and experimentally tested by Borghs *et al.*,[13] the emission intensity is readily calculated,

$$I(h\nu)=B\int_{-\infty}^{\infty}\frac{\rho(E,\eta)}{1+e^{(E-E_F)/kT}}e^{-(E_g+E-h\nu-E_a)^2/w^2}\left[1-\frac{1}{1+e^{(E_g+E-h\nu-E_{Fp})/kT}}\right]dE\ , \tag{2}$$

TABLE I. Parameters for the 2-K near-edge luminescence of virgin sample V and hydrogenated sample H. η is the Kane characteristic energy for the spreading of the conduction-band tail in Eq. (2). n, N_d, and N_a are the free carrier, donor, and acceptor densities, respectively. w is the Gaussian width parameter of the acceptor states in Eq. (2). All energies are in meV, densities in 10^{17} cm^{-3}.

Sample	E_{Fn}	η	$n=N_d-N_a$	N_d	N_a	w
V	17.6	28.1	2.6	7.3	4.7	7.5
H	1.9	19.7	0.8	2.9	2.1	5.3

where E is the electron energy measured from the conduction-band edge, $\eta \propto N_i^{1/2}/n^{1/12}$ is a characteristic energy for the spreading of the conduction-band tail,[14] $n=N_d-N_a$ is the free-carrier density, N_i, N_d, and N_a are the impurity, donor, and acceptor densities, respectively, B is a constant, E_g is the band gap, and E_a is the binding energy of the Si_{As} acceptor. The electron energy E and Fermi level E_F ($\sim$quasi-Fermi level E_{Fn}) are measured from the bottom of the conduction band (>0 above), the hole quasi-Fermi level E_{Fp} from the top of the valence band (>0 above).

Best fittings of the D-A emission bands (and their LO-phonon replicas) at 2 K are shown in Fig. 2(a) for $E_a=34$ meV. The relevant parameters are listed in Table I. The data indicate a passivation of donors and acceptors by a factor of 2.5 and 2.2, respectively. A factor of 2.0 is obtained for the acceptor passivation when this is estimated from the reduction in the acceptor linewidth by using the results known for the C acceptor as an approximate calibration.[15] Although this procedure seems to be quite successful, it suffers from a major drawback: it overlooks many-body effects, in particular exchange and correlation, which are known to give rise to a conspicuous reduction in the band-edge energy. These effects have been tentatively taken into account here in a self-consistent procedure where the gap renormalization as a function of the density of electrons *and* holes has been taken from the work of Vashista and Kalia.[16] Within the rough approximation that the conduction-band shift is equal to the gap renormalization, values for N_d, N_a, and w have been obtained for samples V and H, which are somewhat different with respect to those reported in Table I. Nevertheless, the reduction (equal to four) of active donor concentration estimated in this last approach shows that passivation is anyhow far from being complete.[17]

B. The low-energy range

The appearance, upon hydrogenation, of transitions at higher energy is what one expects if at least one H atom binds at the vacancy. A new stable complex becomes possible, deeper in energy by some 100 meV, if the vacancy charge changes from 3^- to 2^-.[4] We now show quantitatively that this additional transition actually accounts for the different behaviors of samples V and H, explaining in particular the unsatisfactory FWHM fitting in terms of a single Gaussian for the hydrogenated sample in Fig. 3(b).

We start by separating the α band in a lower component α_l and an upper component α_u. As an example, we show in Fig. 4 the 70-K spectrum. By using Gaussian line shapes,[2] we arrive at the T dependence for the integrated emission intensity and FWHM shown in Fig. 5, at the laser-power dependence shown in Fig. 6, and at the T dependence of the peak position shown in Fig. 7. In the last two figures, comparison is made with the behavior of p-type GaAs exposed to a H-ion dose equal to 3.2×10^{19} cm^{-2}. Fitting of the FWHM in terms of Eq. (1a) leads for bands α_u and α_l to the values shown in Table II, where comparison is made with the virgin sample.

Two important features should be underlined. Note that, from Table II and Fig. 5, the lower α band is virtually unchanged by hydrogenation. This is because both the initial and final states of the transition—Si donor and bare V_{Ga}—are the same as for the virgin sample. In n-type material, as a matter of fact, H is not expected to introduce new donors.[5,6] The occurring passivation of some of the Si atoms, as shown by the near-edge behavior, is evidently counterbalanced by an increased efficiency of radiative recombination, due to the passivation of killer centers. The behavior of α_u has instead a peculiarity: from Fig. 6, we see that the ratio α_u/α_l (integrated intensities) for a hydrogenated Si-doped sample decreases for increasing laser power, indicating a rapid saturation of the α_u band. The corresponding ratio for a similarly hydrogenated p-type sample has the opposite trend. This proves that the α_u transition in n-type material, contrary to α_l, does depend critically on the incorporation of H into the vacancy, i.e., that a new, more complex system than the bare V_{Ga}/Si donor, stands behind the α_u transition.

The second argument to the same end comes from comparison to the E_g variation with temperature (Fig. 7).[18] We see that when the shallow excited state in the CC model is associated with the Si donor, for both α_l and α_u the peak shift is opposite to that of E_g. The contrary happens in the H-donor case. These different behaviors can be accounted for in terms of the relevant CC model,

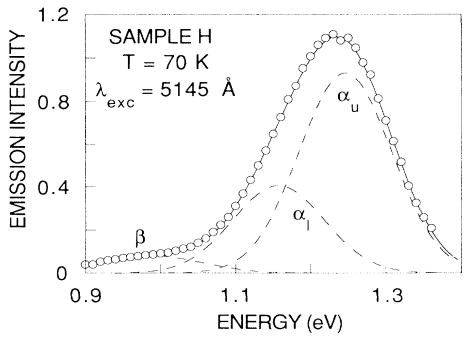

FIG. 4. Deconvolution of the α emission band at 70 K in the hydrogenated sample by means of two Gaussian line shapes overlapping a Gaussian tail from the deeper band β.

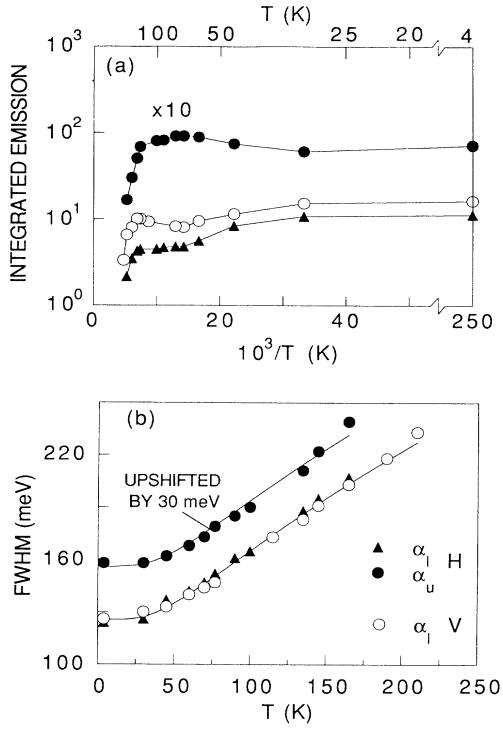

FIG. 5. (a) Integrated emission intensity and (b) FWHM vs temperature for the lower and upper components of the α band, as deduced from deconvolutions of the kind shown in Fig. 4. Solid lines in (a) are guides for the eye, in (b) best-fitting curves from Eq. (1a). Data for the virgin sample from Fig. 3 (empty dots) are shown to demonstrate the virtually unchanged behavior of the lower α band (apart from increased efficiency). Laser exciting power $P=25$ W cm^{-2}.

e.g., by a large coordinate shift Δx for the Si-donor complex as opposed to a small one for the H-donor case.

Therefore, although the V_{Ga}/Si-donor and V_{Ga}/H-donor complexes, in hydrogenated GaAs, present a number of striking similarities—e.g., not too different energy position of the bands, nearly equal vibrational energy in the CC representation—they are totally contrasting as to the temperature and laser power dependences of their

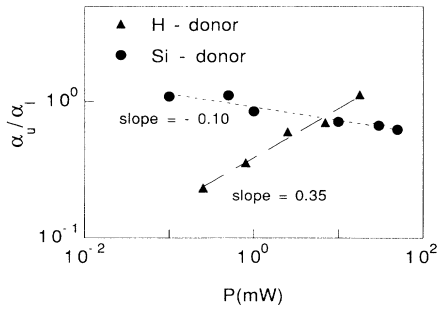

FIG. 6. Ratio of the integrated emission intensity, at 2K, of band α_u to that of band α_l vs laser power for hydrogenated n-type and p-type GaAs. Lines are linear best fits. Hydrogen dose equal to 3.2×10^{19} cm^{-2} for both samples.

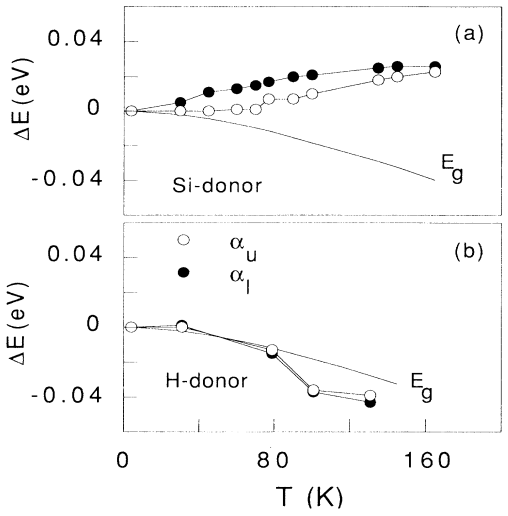

FIG. 7. (a) Shift with temperature of the peak position of bands α_l and α_u for the hydrogenated Si-doped sample, as compared with the E_g variation. (b) The corresponding behaviors of the V_{Ga}/H-donor complexes for the hydrogenated p-type GaAs sample reported in Fig. 6. Lines are guides for the eye. Laser exciting power $P=25$ W cm^{-2}.

peak energy. This is a conclusive argument in favor of the difference in the constituents of the active complex in the two cases, and therefore in the CC model that applies.

C. Reversibility

All the spectral changes introduced by hydrogenation can be fully reversed by annealing at 450 °C for 2 h. It is of immediate conclusion that not only the H atoms which passivate the Si donors leave the active region of the material, as demonstrated by the recovery of the original near-edge emission line shape, but also those which bind at or near a gallium vacancy, whose behavior goes back to that of the untreated sample. H trapped at deep killer centers also seems to be lost, since the total integrated emission goes back to its initial value.

V. CONCLUSIONS

The present twofold experiment in n-type degenerate GaAs—PL near band gap and in the region of gallium vacancy emission, as a function of a number of variables

TABLE II. Main parameters for the α_l (lower) and α_u (upper) bands, for virgin sample V and hydrogenated sample H. All energies are in meV.

Sample	Band	E_{peak} (at 2 K)	A	$h\nu$	T_{quench} (K)
V	α_l	1158	126	11.5	~200
V	α_u	practically missing			
H	α_l	1157	126	11.5	~200
H	α_u	1260	126	11.5	~200

such as T and laser power—proves, in the first place, that hydrogen can be trapped into the vacancy itself, giving rise to novel states of charge and novel optical transitions, much in the same way as earlier reported for moderately n-type or p-type material.[4] In parallel, we have verified that this effect does not prevent passivation of a large fraction of the Si impurities, although this effect turns out to be less strong, for the moment, than one would have hoped for device isolation purposes. Data at 77 K, nevertheless, give very clear evidence of the separation between the donor band and the conduction continuum, produced as a consequence of Si passivation by H.

A remarkable result is that the two Ga-vacancy related emission bands observed here in hydrogenated samples, though associated with the V_{Ga}/Si-donor complex, occur at similar energies and have comparable spectral behavior as the V_{Ga}/H-donor complex, which we have earlier observed in a variety of differently doped and differently produced GaAs.[4]

Another observation is that the large bandwidth and vibrational energy reported by Williams[2] are possibly an artifact resulting from the consideration of a single recombination process for the V_{Ga}-donor band. We suggest that, for some reason, in his material both the lower and the upper level were active due to a mechanism of vacancy decoration other than a post-growth treatment such as hydrogenation.

All the effects can be cycled back to the original behavior by annealing at 450 °C, which rules out defect formation as an alternative explanation for our findings. This is suggestive of the possibility of achieving more efficient binding of H to the Si donors, in case the hydrogenations were effected at a suitably lower temperature than the 300 °C used in the present experiment. Further investigation in this direction is in progress.

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